

The University of Chicago

REACTIONS OF ATOMS AND FREE  
RADICALS IN SOLUTION

- I. REACTIONS OF LEAD TETRAACETATE  
II. RETENTION OF OPTICAL ACTIVITY BY  
FREE RADICALS

A DISSERTATION SUBMITTED TO THE FACULTY  
OF THE DIVISION OF THE PHYSICAL SCIENCES  
IN CANDIDACY FOR THE DEGREE OF DOCTOR  
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY  
JUNE, 1947

By  
HERBERT NORMAN FRIEDLANDER

CHICAGO, ILLINOIS  
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## CONTENTS

### PART I. REACTIONS OF LEAD TETRAACETATE

|                                                        | Page |
|--------------------------------------------------------|------|
| INTRODUCTION . . . . .                                 | 1    |
| Historical Introduction                                |      |
| Reactions of Lead Tetraacetate with Organic Molecules  |      |
| Dehydrogenation Reactions with Lead Tetraacetate       |      |
| The Acetoxylation Reactions of Lead Tetraacetate       |      |
| Compounds containing reactive hydrogen atoms           |      |
| other than olefins                                     |      |
| The reaction of lead tetraacetate with olefins         |      |
| The Glycol Cleavage and Related Reactions of Lead      |      |
| Tetraacetate                                           |      |
| The cleavage reaction with 1,2-dihydroxy com-          |      |
| pounds                                                 |      |
| The reactions of compounds related to the gly-         |      |
| cols with lead tetraacetate                            |      |
| $\alpha$ -Hydroxy acids                                |      |
| Amino derivatives                                      |      |
| $\alpha$ -Keto acids and $\alpha$ -hydroxy ketones     |      |
| Tertiary amino alcohols                                |      |
| The Methylation Reactions of Lead Tetraacetate         |      |
| Proposed Mechanisms of the Reactions of Lead Tetra-    |      |
| acetate                                                |      |
| OBJECT OF PRESENT RESEARCH . . . . .                   | 18   |
| Choice of Reactions Studied                            |      |
| Products of the Decomposition of Lead Tetraacetate     |      |
| in Isopropyl Ether                                     |      |
| Products of the Decomposition of Lead Tetraacetate     |      |
| in Acetic Acid                                         |      |
| A Study of the Kinetics of the Reaction between Lead   |      |
| Tetraacetate and Acetic Acid                           |      |
| DISCUSSION SECTION . . . . .                           | 27   |
| The Reaction of Acetyl Peroxide with Acetic Acid       |      |
| The Reaction of Acetyl Peroxide with Isopropyl Ether   |      |
| The Reaction of Lead Tetraacetate with Isopropyl Ether |      |
| The Reaction of Lead Tetraacetate with Acetic Acid     |      |
| Proposed Mechanism for the Reaction of Lead Tetra-     |      |
| acetate with Organic Compounds                         |      |
| EXPERIMENTAL PART . . . . .                            | 41   |
| Reagents                                               |      |
| Reaction of Lead Tetraacetate with Isopropyl Ether     |      |
| Identification of the High Boiling Ester               |      |
| The Reaction of Lead Tetraacetate with Acetic Acid     |      |
| The Reaction of Lead Tetraacetate and Acetyl Peroxide  |      |
| with Acetic Acid                                       |      |

## CONTENTS--Continued

|                                                                                                                                                      | Page |
|------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| The Rate of Reaction of Lead Tetraacetate with Acetic Acid                                                                                           |      |
| SUMMARY AND CONCLUSIONS . . . . .                                                                                                                    | 46   |
| PART II. THE RETENTION OF OPTICAL ACTIVITY<br>BY FREE RADICALS                                                                                       |      |
| INTRODUCTION . . . . .                                                                                                                               | 47   |
| RESULTS. . . . .                                                                                                                                     | 53   |
| DISCUSSION SECTION . . . . .                                                                                                                         | 53   |
| EXPERIMENTAL PART . . . . .                                                                                                                          | 57   |
| Reagents                                                                                                                                             |      |
| Reaction of <u>d,l</u> - $\alpha$ -Chloroethylbenzene with Normal-Propylmagnesium Bromide in the Presence of Cobaltous Chloride (Five Mole Per Cent) |      |
| Reaction of Levo- $\alpha$ -Chloroethylbenzene with Normal-Propylmagnesium Bromide in the Presence of Cobaltous Chloride                             |      |
| Separation of Active $\alpha$ -Chloroethylbenzene from Inactive 2,3-Diphenylbutane                                                                   |      |
| Reaction of Dextro- $\alpha$ -Chloroethylbenzene with Normal-Propylmagnesium Bromide in the Presence of Cobaltous Chloride                           |      |
| Decomposition of Acetyl Peroxide in <u>d,l</u> - $\alpha$ -Chloroethylbenzene                                                                        |      |
| Decomposition of Acetyl Peroxide in <u>Dextro</u> - $\alpha$ -Chloroethylbenzene                                                                     |      |
| SUMMARY AND CONCLUSIONS . . . . .                                                                                                                    | 62   |



## PART I. REACTIONS OF LEAD TETRAACETATE

### INTRODUCTION

#### Historical Introduction

The fact that minium (the red oxide of lead) reacts with glacial acetic acid was known to the alchemists. But, it was not until 1851 that Jacquelin<sup>1</sup> isolated a white crystalline material from the reaction mixture. And, it remained for Hutchinson and Pollard<sup>2</sup> in 1893 to give lead tetraacetate its correct formula,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ . Lead tetraacetate was not used in organic chemistry until 1920 when Dimroth and his co-workers<sup>3</sup> used lead tetraacetate for certain direct oxidations. For example, they produced pyridine from N, N'-diacetyl-tetrahydro- $\gamma, \gamma'$ -dipyridyl, and anthraquinone from 1,4-dihydroxy-anthraquinone. In these reactions lead tetraacetate acts as a dehydrogenation reagent, removing two hydrogen atoms from the molecule oxidized.

Dimroth<sup>4</sup> also investigated the reactions of lead tetraacetate with various compounds containing reactive hydrogen atoms. In all these reactions the reactive hydrogen atom is replaced by an acetoxyl group. For example, lead tetraacetate reacts with acetic anhydride to give acetoxycetic anhydride.

Criegee<sup>5</sup> continued Dimroth's studies and extended them to unsaturated compounds such as cyclohexene and indene where the lead tetraacetate oxidation takes either or both of two courses: (1) The addition of two acetoxyl groups to the double bond to produce a glycol diacetate. (2) The replacement of a hydrogen atom alpha to the double bond by an acetoxyl group.

---

<sup>1</sup>Jacquelin, J. Prakt. Chem., 53, 151 (1851).

<sup>2</sup>Hutchinson and Pollard, J. Chem. Soc., 63, 1136 (1893).

<sup>3</sup>Dimroth, Friedemann, and Kammerer, Ber., 53, 481 (1920); Dimroth and Frister, Ber., 55, 1231 (1922).

<sup>4</sup>Dimroth and Schweizer, Ber., 56, 1375 (1923).

<sup>5</sup>Criegee, Ann., 481, 263 (1930).

In 1931, Criegee<sup>6</sup> investigated the reaction of glycols with lead tetraacetate. He found that lead tetraacetate causes scission of the carbon to carbon bond between the two atoms holding the hydroxyl group with the production of the corresponding carbonyl compounds from the fragments. For example, ethylene glycol when treated with lead tetraacetate gives two molecules of formaldehyde. After Criegee's discovery, the glycol cleavage reactions by lead tetraacetate was used extensively to study the configurations of many natural occurring products containing adjacent hydroxyl groups, and in determining the structures of sugars and other saccharides.

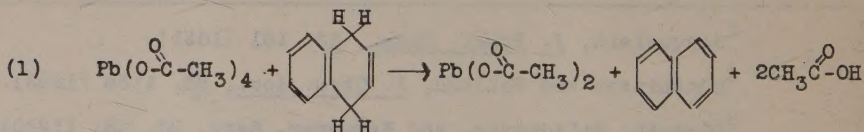
Fieser<sup>7</sup> discovered that lead tetraacetate methylates certain aromatic compounds. Thus, trinitrometaxylene can be made from trinitrotoluene; and, 2,3-dimethyl-1,4-naphthaquinone can be made from 2-methyl-1,4-naphthaquinone.

#### Reactions of Lead Tetraacetate with Organic Molecules

The reactions of lead tetraacetate with organic molecules can be divided into four classes: (1) dehydrogenation, (2) acetoxylation, (3) glycol cleavage, (4) methylation.

##### Dehydrogenation Reactions with Lead Tetraacetate

Table 1 lists some of the typical compounds which undergo dehydrogenation when treated with lead tetraacetate. The yields of the final products and the general reaction conditions are also indicated. Specifically, the reaction is suitable for the preparation of aromatic compounds from their dihydro compounds and aldehydes and ketones from alcohols. The nature of this reaction is illustrated by the stoichiometric equations: (1) for 1,4-dihydronaphthalene,




---

<sup>6</sup>Criegee, Ber., 64, 260 (1931).

<sup>7</sup>Fieser and Chang, J. Am. Chem. Soc., 64, 2043 (1942); Fieser, Clapp, and Daudt, ibid., 64, 2052 (1942); Fieser and Oxford, ibid., 64, 2060 (1942).

TABLE 1

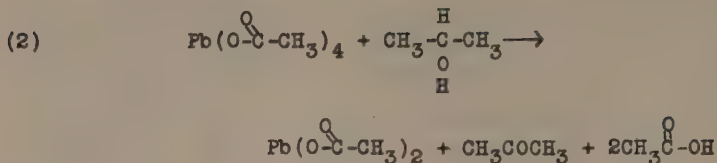
## DEHYDROGENATION REACTION WITH LEAD TETRAACETATE

| Compound                                                      | Products and Yields                            | Temperature | Time                                                           | Solvent          | Reference |
|---------------------------------------------------------------|------------------------------------------------|-------------|----------------------------------------------------------------|------------------|-----------|
| N,N'-diacetyl<br>dihydro- $\delta, \delta'$ -<br>dipyridyl    | $\delta, \delta'$ -dipyridyl, 90%              | 20°         | very fast                                                      | acetic anhydride | a         |
| N,N'-diacetyl<br>tetra-hydro-<br>$\delta, \delta'$ -dipyridyl | pyridine, 90%                                  | 20°         | very fast                                                      | acetic anhydride | a         |
| 1,4-dihydro<br>naphthalene                                    | naphthalene, 65%                               | 20°         | several hours                                                  | acetic acid      | b         |
| 9,10-dihydro<br>anthracene                                    | anthracene, 30%                                | 80°         | 1 hour                                                         | benzene          | b         |
| ethyl alcohol                                                 | acetaldehyde, 89%                              | 20°         | 1 day                                                          | ethyl alcohol    | c         |
| isopropanol                                                   | acetone, 96%                                   | 20°         | 1/4 hour                                                       | isopropanol      | c         |
| 1,4-dihydroxy<br>anthraquinone                                | anthraquinone, 65%                             | 20°         | 5 minutes                                                      | acetic acid      | d         |
| tetralin hydro-<br>peroxide                                   | $\alpha$ -tetralone, 80%<br>and O <sub>2</sub> | < 30°       | add lead tetra-<br>acetate drop-<br>wise reacts<br>immediately | acetic acid      | e         |

<sup>a</sup>Dimroth and Frister, Ber., 55, 1231 (1922). <sup>b</sup>Criegee, Ann., 481, 263 (1930).<sup>c</sup>Criegee, Kraft, and Rank, Ann., 507, 159 (1933).<sup>d</sup>Dimroth, Friedemann, and Kemmerer, Ber., 53, 481 (1920).<sup>e</sup>Criegee, Pilz, and Flygare, Ber., 72, 1799 (1939).



and (2) for isopropanol,

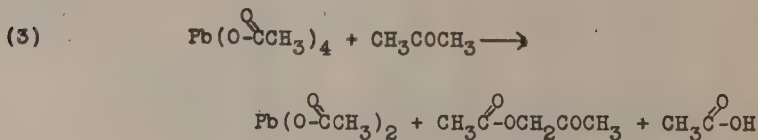


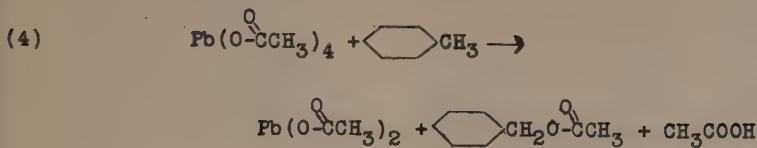
In each case one molecule of lead tetraacetate removes two hydrogen atoms from the molecule oxidized yielding lead diacetate and two molecules of acetic acid. Not all hydrogenated aromatic compounds are dehydrogenated since the double bonds in the molecule may compete by reaction with the lead tetraacetate to form acetoxy compounds. For example, 1,2-dihydronaphthalene yields only 20% naphthalene, the major product being 1,2-diacetoxynaphthalin. The oxidation of tetralin hydroperoxide to tetralone and oxygen is a novel variation of the dehydrogenation reaction. It is to be noted from Table 1 that the rate of reaction of lead tetraacetate varies greatly from compound to compound. This will also be true of the other reactions of lead tetraacetate.

#### The Acetoxylation Reactions of Lead Tetraacetate

Lead tetraacetate reacts with compounds containing reactive hydrogen atoms to replace the hydrogen atom by acetoxy groups.

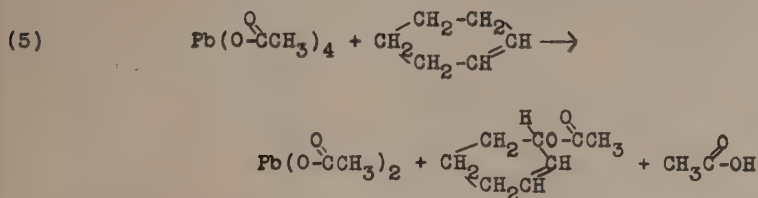
Compounds containing reactive hydrogen atoms other than olefins. --Lead tetraacetate reacts with compounds such as acetic anhydride, malonic acid, acetone, acetophenone, toluene, diphenyl methane, tetralin, and acetoacetic ester to replace the active hydrogen atoms by acetoxy groups. Table 2, Part A, lists some of the typical compounds containing reactive hydrogen atoms, other than olefins, which undergo the acetoxylation reaction. Equations 3 and 4 illustrate the acetoxylation reaction for acetone and for toluene.



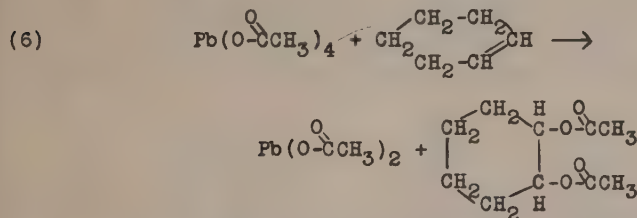


The other reaction products are lead diacetate and acetic acid. Note that the rate of reaction of lead tetraacetate varies greatly from compound to compound.

The reaction of lead tetraacetate with olefins.--Table 2, Part B, lists some of the olefins which react with lead tetraacetate and the yields of products and general reaction conditions wherever these are described in the literature. Olefins undergo two major types of reactions and one side reaction with lead tetraacetate. The first of these is the replacement of a reactive hydrogen atom alpha to the double bond by an acetoxyl group. Thus cyclohexene gives 3-acetoxycyclohexene-1.



This type of reaction is similar to the reaction of olefins with peracids, oxygen (in auto-oxidations) and other oxidizing agents.<sup>8</sup> The reactions cited above are considered to proceed by a free radical mechanism. The second major mode of attack consists of addition of two acetoxyl groups to the double bond as illustrated for cyclohexene.



<sup>8</sup>Farmer, Trans. Farad. Soc., 38, 300, 348 (1942).

TABLE 2

## THE ACETOXYLATION REACTION OF LEAD TETRAACETATE

| Compound                                                                | Products and Yields                                                                  | Temperature | Time         | Solvent          | Reference |
|-------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-------------|--------------|------------------|-----------|
| Part A. Compounds Containing Reactive Hydrogen Atoms Other Than Olefins |                                                                                      |             |              |                  |           |
| acetic anhydride                                                        | O-acetyl-glycolic acid anhydride 40%<br>some CO <sub>2</sub> , 5% hydro-carbon gases | 140°        | 1/4-1/2 hour | acetic anhydride | a         |
| acetone                                                                 | monoacetoxyacetone 30%<br>diacetoxyacetone                                           | 70-80°      | 7 hours      | acetic acid      | a         |
| acetoacetic ester                                                       | acetoxy-acetoacetic ester 45%                                                        | 45°         | very fast    | acetic acid      | a         |
| acetoacetic ester                                                       | acetoxy-acetoacetic ester 60%                                                        | 35°         | very fast    | benzene          | a         |
| toluene                                                                 | benzyl acetate 20%                                                                   | 111°        | 4 hours      | acetic acid      | a         |
| diphenyl methane                                                        | diphenylcarbinol acetate 40%                                                         | 120°        | 1 hour       | acetic acid      | a         |
| 20-methyl cholanthrene                                                  | 15-acetoxy-20-methyl cholanthrene 46%<br>15-keto-20-methyl cholanthrene 7%           | 15°         | 6 hours      | acetic acid      | b         |
| 1,2-benzanthrene                                                        | 1,2-benzanthrene-10-acetate 69%                                                      | 100°        | 15 minutes   | acetic acid      | b         |
| tetralin                                                                | 1-acetoxy-tetralin 33%                                                               | 90-100°     | 1 hour       | acetic acid      | c         |

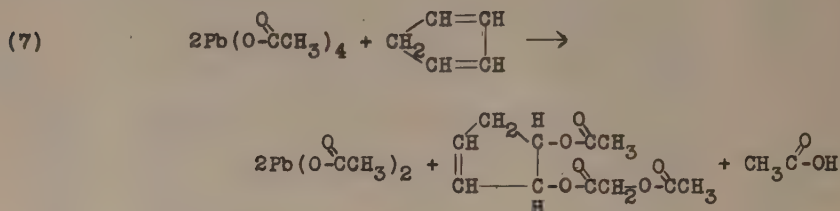


TABLE 2--Continued

| Compound                | Products and Yields                                                                                     | Temperature | Time      | Solvent     | Reference |
|-------------------------|---------------------------------------------------------------------------------------------------------|-------------|-----------|-------------|-----------|
| Part B. Olefins         |                                                                                                         |             |           |             |           |
| anethole                | diacetox-y-anethole                                                                                     | 40°         | 1-2 hours | acetic acid | a         |
| cyclohexene             | 3-acetox-y-cyclo-hexene-1 29%<br>1,2-diacetox-y cyclo-hexane 9%<br>traces unsat. diacetox-y derivatives | 80°         | 3 hours   | acetic acid | c         |
| cyclopenta-diene        | 3-acetox-y-4-0-acetyl-glycoxcyclopentene-1 28%<br>3,4-diacetox-y-cyclo-pentene-1 10%                    | 20°         | very fast | acetic acid | c         |
| 1,2-dihydro naphthalene | naphthalene 20% and 1,2-diacetox-y-tetralin 48%                                                         | 70°         | 1 hour    | acetic acid | c         |
| 2,3-dimethyl butadiene  | 1,2-diacetox-y-2,3-dimethyl-butene-3 37%                                                                | 60°         | 1/2 hour  | acetic acid | c         |
| 1-phenyl-1, 2-butadiene | diacetate addition compound                                                                             | 50°         | 4-5 hours | acetic acid | d         |

<sup>a</sup>Dimroth and Schweizer, Ber., 56, 1375 (1923).<sup>b</sup>Pfieser and Hershberg, J. Am. Chem. Soc., 60, 1893, 2542 (1938).<sup>c</sup>Criegee, Ann., 481, 263 (1930). <sup>d</sup>La Forge and Acree, J. Org. Chem., 6, 208 (1941).

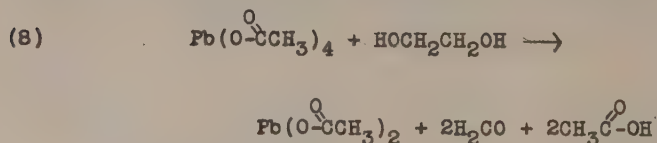
Cyclopentadiene does not undergo the reaction cited in equation (5) but undergoes a "side" reaction. This "side" reaction consists of the replacement by an acetoxyl group of one of the hydrogen atoms alpha to the carboxyl group forming a glycolic acid derivative. However, cyclohexene does not undergo the "side" reaction. Equation 7 illustrates the "side" reaction for cyclopentadiene.



Similar "side" reactions have been observed with lead tetrapropionate, lead tetrabutyrates, but not with lead tetrabenzoate. In the case of the latter compound no glycolic acid type derivatives are possible since there are no hydrogen atoms alpha to the carboxyl group. In the reaction with olefins again we note that the reaction conditions vary greatly from compound to compound.

#### The Glycol Cleavage and Related Reactions of Lead Tetraacetate

The cleavage reaction with 1,2-dihydroxy compounds.--It is interesting to note that the diacetoxyl compounds produced from olefins do not react further with lead tetraacetate, although on hydrolysis they yield glycols which do react rapidly with lead tetraacetate undergoing scission of a carbon to carbon bond with the production of the corresponding carbonyl compounds of both fragments. Equation 8 illustrates this reaction.

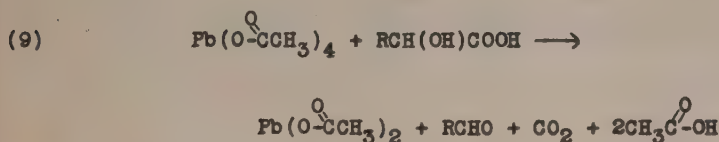


The reaction of lead tetraacetate with 1,2-dihydroxy com-

pounds is unique because of the following facts:<sup>9</sup> (1) A carbon to carbon bond of the 1,2-glycol molecule is broken under mild reaction conditions. On the other hand, monohydroxy compounds or 1,3-dihydroxy compounds are only slowly attacked, under similar treatment with lead tetraacetate, to give oxidation products where the carbon chain is untouched (compare the dehydrogenation reaction already discussed for simple alcohols). (2) The reaction is rapid at room temperature and is nearly quantitative. Thus, the yields of formaldehyde from ethylene glycol are about 95%. There is, however, considerable variation of reaction rate among glycols. Thus, cis-dihydroxycyclopentane reacts several hundred times faster than diethyl tartarate which reacts about one hundred times faster than ethylene glycol. (3) No cleavage of glycols occur if one or both of the hydrogen atoms of the hydroxyl groups are replaced by acyl or alkyl groups. (4) Cis glycols react more rapidly than the corresponding trans glycols. This is particularly noticeable in the behavior of 1,2-cyclopentanediols which have a rigid ring as compared to the 1,2-cyclohexanediols where there is less rigidity in the ring. The difference in rate between cis and trans glycols has been useful in determining configurations of sugars and other natural products. The glycol cleavage reaction has been useful in determining the structures of many natural products containing glycol groups or capable of being oxidized or reduced to compounds containing glycol groups. See Table 3 listing typical compounds which undergo cleavage.

The reactions of compounds related to the glycols with lead tetraacetate.--

$\alpha$ -Hydroxy acids.-- $\alpha$ -Hydroxy acids undergo a similar reaction with lead tetraacetate.<sup>10</sup>



The radical R is either methyl, isobutyl, phenyl, or benzyl radical.

<sup>9</sup>Criegee, Kraft, and Rank, Ann., 507, 157 (1933).

<sup>10</sup>Haruomi Oeda, Bull. Chem. Soc. Japan, 9, 8 (1934); Chem. Abst., 28, 2700 (1934).



TABLE 3  
THE GLYCOL SPLITTING REACTION OF LEAD TETRAACETATE

| Compound              | Products and Yields                        | Temperature | Time            | Solvent                            | Reference |
|-----------------------|--------------------------------------------|-------------|-----------------|------------------------------------|-----------|
| ethylene glycol       | formaldehyde 95%                           | 20°         | 20 hours        | acetic acid                        | a         |
| diethyl tartarate     | ethyl glyoxalate 95%                       | 40-50°      | 1/4 hour        | acetic acid                        | a         |
| pinacol               | acetone 91%                                | 40-50°      | 1/4 hour        | acetic acid                        | a         |
| pinacol               | acetone 95%                                | 20°         | extremely rapid | acetic acid plus water or methanol | b,c       |
| phenyl-glyoxylic acid | benzoic acid 96.7% and CO <sub>2</sub> 95% | 40-50°      | very rapid      | acetic acid plus water             | d         |
| benzoïn               | benzil 83.4%                               | 50°         | 24 hours        | acetic acid no water               | d         |
| benzoïn               | benzaldehyde 75% and benzoic acid 74%      | 20°         | very rapid      | acetic acid plus water             | d         |

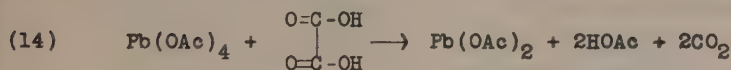
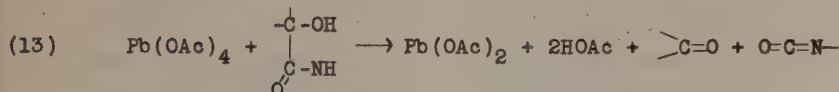
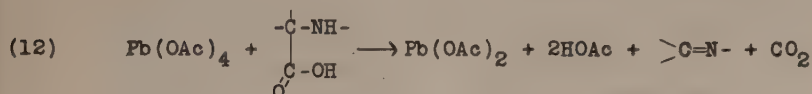
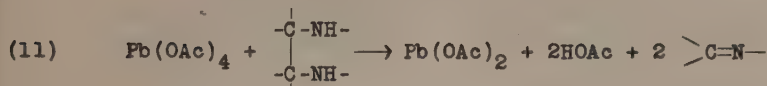
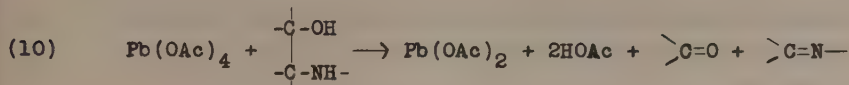
<sup>a</sup>Criegee, Ber., 64, 260 (1931).

<sup>b</sup>Baer, Grosheintz, and Fisher, J. Am. Chem. Soc., 61, 2607 (1939).

<sup>c</sup>Criegee and Buchner, Ber., 73, 563 (1940).

<sup>d</sup>Baer, J. Am. Chem. Soc., 62, 1597 (1940).

Amino derivatives.--Criegee, Kraft, and Rank<sup>11</sup> list a number of other compounds besides 1,2-dialcohols and  $\alpha$ -hydroxy acids, which would be expected to undergo the carbon to carbon cleavage. Equations 10 to 14 list these compounds and their products. OAc is an abbreviation for  $\text{OOCCH}_3$  and the unfilled valences represent any common radical or hydrogen.

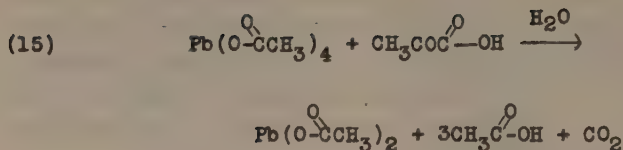


Under the condition of the reaction the nitrogen containing products would probably undergo further reaction. No experimental data, however, is given by Criegee.

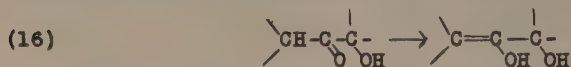
$\alpha$ -Keto acids and  $\alpha$ -hydroxy ketones.--Baer<sup>12</sup> states that water or methanol increases the rate of the glycol reaction in acetic acid solution. In the presence of water the reaction with lead tetraacetate can be extended to cover the reaction with  $\alpha$ -keto acids and  $\alpha$ -hydroxy ketones. This reaction is illustrated for pyruvic acid.

<sup>11</sup>Criegee, Kraft, and Rank, op. cit.

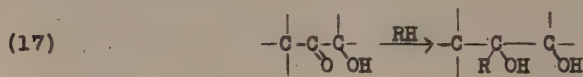
<sup>12</sup>Baer, Grosheintz, and Fischer, J. Am. Chem. Soc., 61, 2607 (1939); Baer, ibid., 62, 1597 (1940); cf. Criegee and Buchner, Ber., 73, 563 (1940).



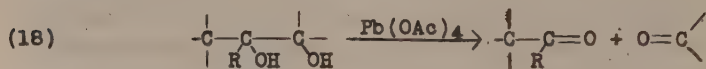
Two explanations have been offered to account for the effect of water: (1) enolization (reaction 16)



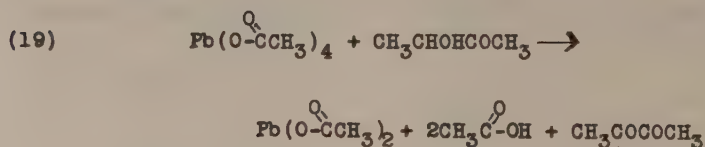
and (2) solvolysis (reaction 17),



R is HO-, CH<sub>3</sub>O-, C<sub>2</sub>H<sub>5</sub>O-, C<sub>6</sub>H<sub>5</sub>O-, or CN-. Baer prefers the solvolysis explanation since the reaction occurs with compounds that cannot enolize and does not occur in the absence of water with compounds that enolize. Furthermore, if the R group is alkoxy or cyano the corresponding esters or alpha keto nitriles are formed as shown in reaction 18.

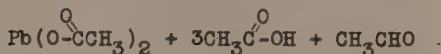
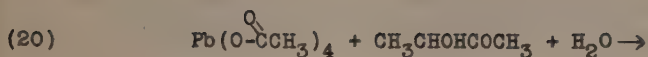


α-Hydroxy ketones on the other hand are slowly oxidized (compare the dehydrogenation reaction) to diketones in the absence of water.



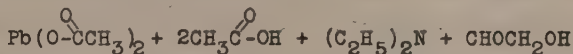
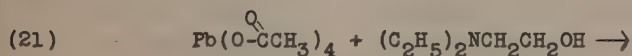
Upon addition of water, however, a rapid reaction ensues resulting in rupture of the carbon to carbon bond and the formation of an acid and the corresponding carbonyl compound.





From the fact that in the absence of water  $\alpha$ -hydroxy ketones are oxidized to 1,2-diketones, which are not attacked rapidly by lead tetraacetate, we must conclude that neither of these molecular species are intermediates in the scission of glycols. See Table 3 for data on compounds undergoing these reactions.

Tertiary amino alcohols.--Leonard and Rebenstorf,<sup>13</sup> in studies of tertiary amino alcohols obtained rupture of the carbon to nitrogen bond instead of a carbon to carbon bond. In this respect the reaction is different than the glycol cleavage reactions of 1,2-primary and secondary amino alcohols and diamines. Thus, 2-hydroxyethyl-diethylamine gives diethylamine and glyoxal.



Furthermore, the specificity was not confined to 1,2-tertiary amino alcohols. Any tertiary amino alcohol gave the same products, namely, a secondary amine and a hydroxy aldehyde. For example, 4-hydroxybutyl-diethylamine gave diethylamine and 4-hydroxybutyraldehyde. These reactions were run at 60°C in acetic acid solution, and required from one-half to four days for complete utilization of the lead tetraacetate. From triethylamine a trace of diethylamine could be isolated after 4 days reaction at 60°C, at which time some unreacted lead tetraacetate still remained.

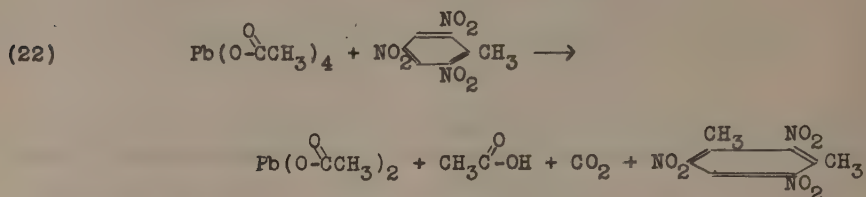
#### The Methylation Reactions of Lead Tetraacetate

Fieser and his co-workers<sup>14</sup> found that lead tetraacetate

<sup>13</sup> Leonard and Rebenstorf, J. Am. Chem. Soc., **67**, 49 (1945).

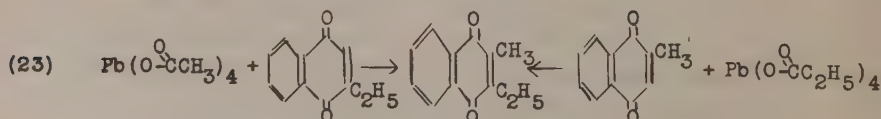
<sup>14</sup> Fieser and Chang, op. cit.; Fieser, Clapp, and Daudt, op. cit.; Fieser and Oxford, op. cit.

could be used to methylate the aromatic ring in certain aromatic compounds, particularly naphthaquinones and nitrobenzenes.



These reactions were run in acetic acid solution. Fieser also found that he could obtain the same results using acetyl peroxide. The methylation reaction was unique for two reasons: (1) In order to obtain a 30% yield of the methylated compounds a 3-4 mole excess of lead tetraacetate was needed, although one mole of acetyl peroxide was sufficient to produce the same yield. (2) In the presence of certain promoters (in general compounds containing active hydrogens such as malonic acid, methanol, water, isopropanol, cyclohexane, isopropyl ether, benzene, and octane), the methylation reactions went more quickly and at lower temperatures. Thus four hours were required at 50° in the presence of a promoter, while in the absence of a promoter 20 hours was required at 100°. However, any reaction that would go in the presence of the promoters would also go in their absence. Furthermore, the promoters themselves reacted with lead tetraacetate giving carbon dioxide and hydrocarbon gases. The fact that these promoters react with lead tetraacetate is not surprising since they belong to the classes of substances known to undergo the acetoxylation or dehydrogenation reaction.

Fieser showed that the methyl radical in these methylation reactions comes from the lead tetraacetate. He methylated 2-ethyl-1,4-naphthaquinone with lead tetraacetate and obtained 2-methyl-3-ethyl-1,4-naphthaquinone. Whereas when 2-methyl-1,4-naphthaquinone was reacted with lead tetrapropionate 2-methyl-3-ethyl-1,4-naphthaquinone was again obtained.

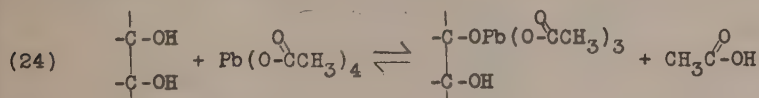


It is interesting to note that many of the reactions discussed here use acetic acid as a solvent. The possibility of a reaction between lead tetraacetate and acetic has been ignored by most authors, in spite of the fact that Dimroth<sup>15</sup> reported a 2.6% utilization of the lead tetraacetate after one-and-three-quarters hours at the boiling point of acetic acid. In the present study it was found that eight to twelve hours were required for complete utilization of the lead tetraacetate. Dimroth<sup>16</sup> also showed that only a 1% reaction occurs with benzene after five-and-one-half hours at 78°, whereas Fieser<sup>17</sup> was able to utilize the lead tetraacetate more completely. The formation of benzyl acetate from benzene is interpreted on the basis that the benzene is first methylated to toluene which then gives the benzyl acetate by acetoxylation.

Furthermore, it has been found<sup>18, 19</sup> that in acetic acid solution lead tetraacetate can be replaced by red lead. Although this procedure is somewhat more simple experimentally, it does not give as good yields as does purified lead tetraacetate.

#### Proposed Mechanisms of the Reactions of Lead Tetraacetate

No mechanisms have been proposed for the dehydrogenation reactions with lead tetraacetate nor for the acetoxylation reactions. For the glycol cleavage reactions Criegee postulated the following mechanism to account for the rapidity of the reactions under mild conditions, the specificity for free hydroxyl groups, and the more rapid reactions of cis than trans glycols.



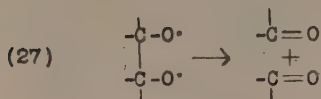
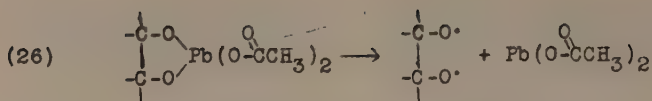
<sup>15</sup>Dimroth and Schweizer, op. cit.

<sup>16</sup>Ibid.

<sup>17</sup>Fieser and Chang, op. cit.; Fieser, Clapp, and Daudt, op. cit.; Fieser and Oxford, op. cit.

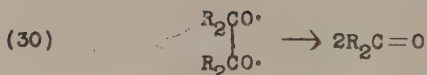
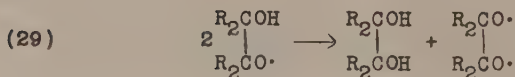
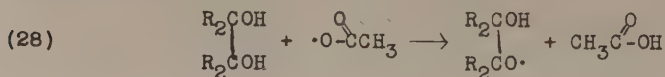
<sup>18</sup>Ibid.

<sup>19</sup>Ward, J. Am. Chem. Soc., **60**, 325 (1938).



Reaction 24 is assumed by Griegee since he was able to replace an acetoxyl group by a methoxyl group. This he accomplished by the interaction of lead tetraacetate with methanol. Reaction 25 is considered the rate determining step. This hypothesis explains the difference in reaction rate between cis and trans 1,2-glycols. Furthermore, the mechanism postulated suggests that in acetic acid solution the reaction should be first order with respect to both the glycol and the lead tetraacetate. In other solvents such as benzene the rate should be inversely proportional to the acetic acid concentration. Griegee has shown this to be true.<sup>20</sup> The last two steps (reactions 26 and 27) are presumably very fast.<sup>21</sup>

Based on Fieser's methylation reaction, Waters<sup>22</sup> postulates that in the oxidation of glycols the first step is the breakdown of lead tetraacetate to form free acetoxyl and free methyl radicals which then react as indicated below:



<sup>20</sup>Griegee, Kraft, and Rank, op. cit.

<sup>21</sup>Griegee, Ber., **68**, 665 (1935).

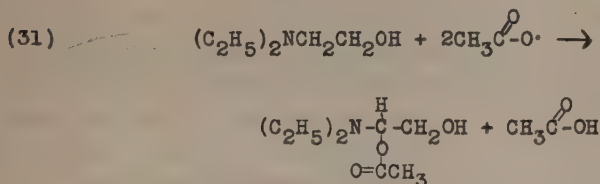
<sup>22</sup>Waters, J. Chem. Soc., **1946**, 409; Trans. Farad. Soc., **42**, 184 (1946).



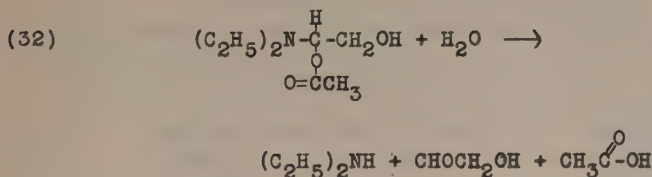
In support of this hypothesis Waters cites the action of lead tetraacetate in the auto-oxidation of tetralin, and compares the effect with that produced by many other substances capable of producing free radicals.

This theory, however, fails to account for the difference of reaction rates between the *cis* and *trans* glycols.

For the reaction of tertiary amino alcohols with lead tetraacetate, Leonard and Rebenstorf<sup>23</sup> postulate the initial decomposition of lead tetraacetate to free acetoxyl radicals. A free acetoxyl radical is postulated to replace a hydrogen atom alpha to the amino group which was previously removed by another free acetoxyl radical (see equation 31).



On subsequent hydrolysis the postulated addition compound breaks down to give the secondary amine and hydroxy aldehyde found.



Fieser,<sup>24</sup> because of the similar methylation reactions of acetyl peroxide, considers as a possible mechanism for the methylation reactions with lead tetraacetate either that the lead tetraacetate forms acetyl peroxide which then breaks down to form methyl and acetoxyl free radicals or forms these free radicals directly.

<sup>23</sup> Leonard and Rebenstorf, op. cit.

<sup>24</sup> Fieser and Chang, op. cit.; Fieser, Clapp, and Daudt, op. cit.; Fieser and Oxford, op. cit.

## OBJECT OF PRESENT RESEARCH

### Choice of Reactions Studied

Waters<sup>25</sup> considers that lead tetraacetate in solution breaks down into the same free radicals as are found in the decomposition of acetyl peroxide in solution. In order to test this hypothesis the reactions of lead tetraacetate with isopropyl ether and acetic acid were studied. These two solvents were picked because careful study had been made of their reactions with acetyl peroxide and a comparison of the reaction products between that reagent and lead tetraacetate were therefore at hand. Furthermore, as a result of the studies with acetyl peroxide, it was found that isopropyl ether was useful in detecting free acetoxyl radicals and that acetic acid was useful in detecting free methyl radicals. Isopropyl ether was one of the compounds Fieser<sup>26</sup> used as a promoter for the methylation reactions of lead tetraacetate. Thus it was hoped that a study of the reaction of lead tetraacetate with isopropyl ether would give more information concerning the mechanism of the methylation reaction.

### Products of the Decomposition of Lead Tetraacetate in Isopropyl Ether

Isopropyl ether was chosen because of its usefulness in the study of acetoxyl free radicals as born out by the decomposition of acetyl peroxide in that solvent.<sup>27</sup> Table 4 lists the products of the reaction of lead tetraacetate and acetyl peroxide with isopropyl ether at its boiling point. A detailed analysis of these two reactions will be given in the discussion section.

### Products of the Decomposition of Lead Tetraacetate in Acetic Acid

The reaction of lead tetraacetate in acetic acid shows a much different course than that of acetyl peroxide in the same solvent.<sup>28</sup> Table 5 lists the products of the decomposition of

<sup>25</sup>Waters, op. cit.

<sup>26</sup>Fieser and Chang, op. cit.; Fieser, Clapp, and Daudt, op. cit.; Fieser and Oxford, op. cit.

<sup>27</sup>Kharasch and Fineman, Unpublished results.

<sup>28</sup>Kharasch and Gladstone, J. Am. Chem. Soc., 65, 15 (1943).

TABLE 4

PRODUCTS OF THE DECOMPOSITION OF LEAD TETRAACETATE AND  
ACETYL PEROXIDE IN ISOPROPYL ETHER

| Reactants                                       | Moles                          | Moles                      |
|-------------------------------------------------|--------------------------------|----------------------------|
| isopropyl ether                                 | 13                             | 9                          |
| lead tetraacetate                               | 1                              | .....                      |
| acetyl peroxide                                 | .....                          | 1                          |
| Products                                        | Moles/Mole Lead Tetraacetate   | Moles/Mole Acetyl Peroxide |
| lead diacetate                                  | 1.0                            | .....                      |
| carbon dioxide                                  | 0.16                           | 0.85                       |
| methane                                         | 0.16                           | 0.76                       |
| acetic acid                                     | 1.36                           | 0.92                       |
| acetone                                         | 0.004                          | 0.14                       |
| isopropanol                                     | 0.005                          | 0.16                       |
| isopropyl acetate                               | 0.01                           | 0.23                       |
| 1-methyl-1-isopropoxy-ethylene-glycol diacetate | 0.17                           | .....                      |
| formaldehyde                                    | trace                          | .....                      |
| Residue                                         | 7 Grams/Mole Lead Tetraacetate | 21 Grams/Mole Peroxide     |

TABLE 5  
PRODUCTS OF THE DECOMPOSITION OF LEAD TETRAACETATE AND ACETYL PEROXIDE IN ACETIC ACID

| Reactants               | Moles                           | Moles                                        | Moles                      | Moles                                          | Moles                           |
|-------------------------|---------------------------------|----------------------------------------------|----------------------------|------------------------------------------------|---------------------------------|
| acetic acid             | 14                              | 14                                           | 35                         | 10                                             | 17                              |
| lead tetraacetate       | 1                               | 1                                            | .....                      | 0.535                                          | 1                               |
| acetyl peroxide         | .....                           | .....                                        | 1                          | 0.465                                          | .....                           |
| acetoxyacetic acid      | .....                           | .....                                        | .....                      | .....                                          | 1                               |
| Temperature of Reaction | 118°                            | 128°                                         | 90°                        | 90°                                            | 80°                             |
| Products                | Moles/Mole Lead Tetraacetate    | Moles/Mole Lead Tetraacetate                 | Moles/Mole Acetyl Peroxide | Moles/Mole Lead Tetraacetate + Acetyl Peroxide | Moles/Mole Lead Tetraacetate    |
| lead diacetate          | 1.0                             | 1.0                                          | .....                      | 0.54                                           | 1.0                             |
| carbon dioxide          | 0.42                            | 0.31                                         | 1.52                       | 1.24                                           | 0.46                            |
| methane                 | 0.30                            | 0.26                                         | 1.47                       | 0.75                                           | 0.27                            |
| methyl acetate          | none                            | none                                         | 0.05                       | 0.03                                           | none                            |
| acetoxyacetic acid      | 0.40                            | 0.50                                         | none                       | 0.002                                          | 1.23 <sup>a</sup>               |
| succinic acid           | trace                           | no trace found                               | 0.50                       | 0.05                                           | trace                           |
| methylene diacetate     | 0.06                            | 0.001                                        | none                       | 0.02                                           | 0.12                            |
| formaldehyde            | trace                           | trace                                        | .....                      | trace                                          | trace                           |
| residue                 | 22 grams/mole lead tetraacetate | 16 grams/mole lead tetraacetate <sup>b</sup> | .....                      | 7 grams/mole                                   | 19 grams/mole lead tetraacetate |

<sup>a</sup>That is an increase of 0.23 moles/mole lead tetraacetate over the initial amount.

<sup>b</sup>In this one case where the residue was investigated, it was found that, of the 16 grams/mole, 9.5 grams/mole consisted of lead salts. Undoubtedly the other residues contained a large proportion of heavy lead salts which accounts for their apparent large size.



lead tetraacetate and acetyl peroxide in acetic acid.

An exploratory run was made of the decomposition of lead tetraacetate in methylene diacetate. The reaction was considerably slower than the decompositions in acetic acid or isopropyl ether. The amount of carbon dioxide in excess to methane was considerably greater than in the runs with the other two solvents.

#### A Study of the Kinetics of the Reaction between Lead Tetraacetate and Acetic Acid

In order to elucidate further the details of the reaction between lead tetraacetate and acetic acid, a number of studies were undertaken in which the rate of disappearance of lead tetraacetate was measured. The data are to be found in Graphs Ia, IIa, Ib, and IIb.

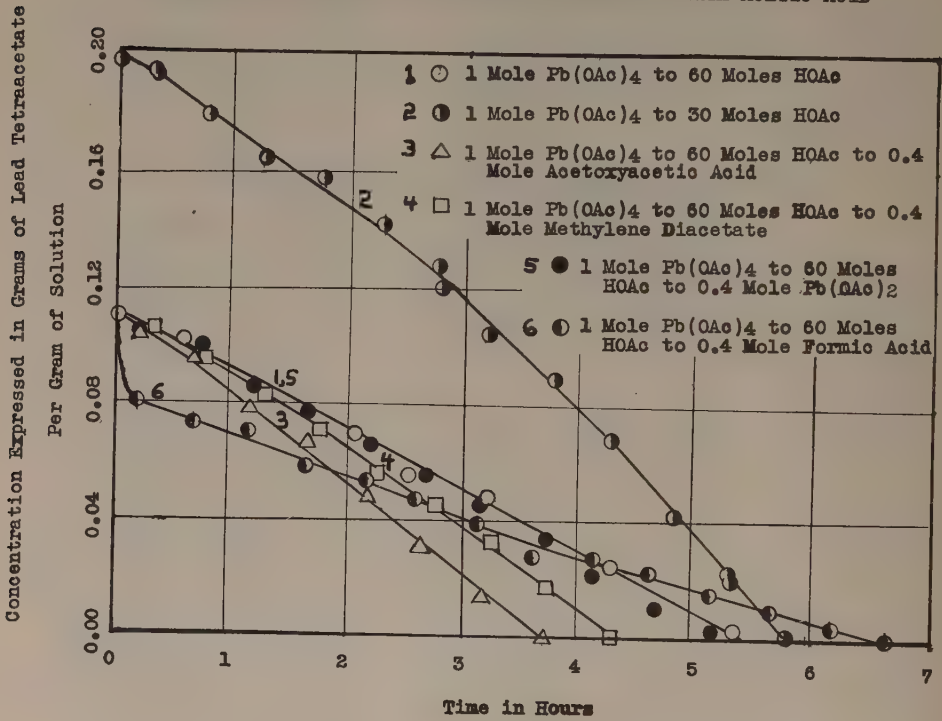
It was found that different batches of lead tetraacetate gave different curves under the same reaction conditions (compare curves 1 and 7). Since lead tetraacetate is recrystallized from hot acetic acid with which it reacts slowly, the non-reproducibility was found to depend on the time taken to recrystallize the lead tetraacetate. There is some unavoidable reaction of the lead tetraacetate with the hot acetic acid during recrystallization. Impurities in the form of lead salts in which acetoxyacetic acid replaces some of the acetic acid are formed during recrystallization. These impurities affects the rate of the reaction.

A summary of the experimental conditions used in the kinetic studies is given in Table 6.

An analysis of the kinetic data indicate that the decomposition of lead tetraacetate in acetic acid is very complicated and does not follow a simple reaction order. The concentration versus time curves (graphs Ia and IIa) are almost linear giving the appearance of a zero order reaction. However, the reaction is not zero order since the rate of disappearance, thereby the slope of the curve, is not independent of the initial concentration (compare curves 1 and 2). The logarithm of the concentration versus time curves (graphs Ib and IIb) show a somewhat linear portion near the beginning of a reaction as would be expected for a first order reaction and a rapidly dropping portion at the end. This behavior shows that the reaction is of no simple order but rather of some complex mixed order. Such a behavior is that to be expected from a reaction where the reaction products react with lead

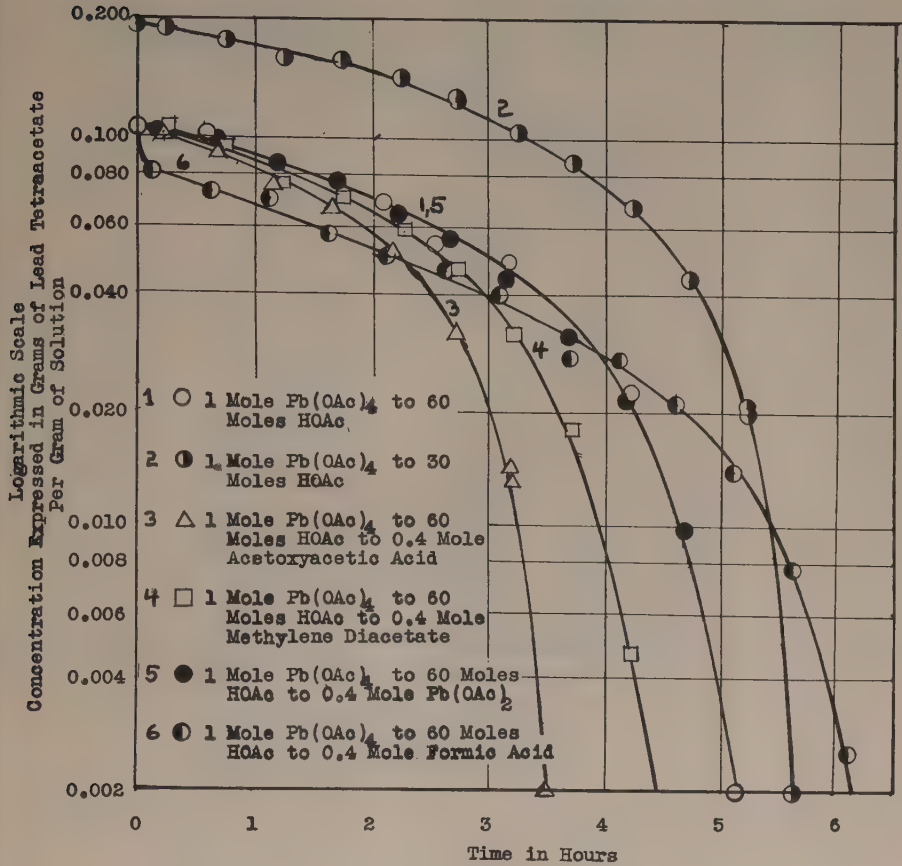
GRAPH Ia

KINETICS OF THE REACTION OF LEAD TETRAACETATE WITH ACETIC ACID



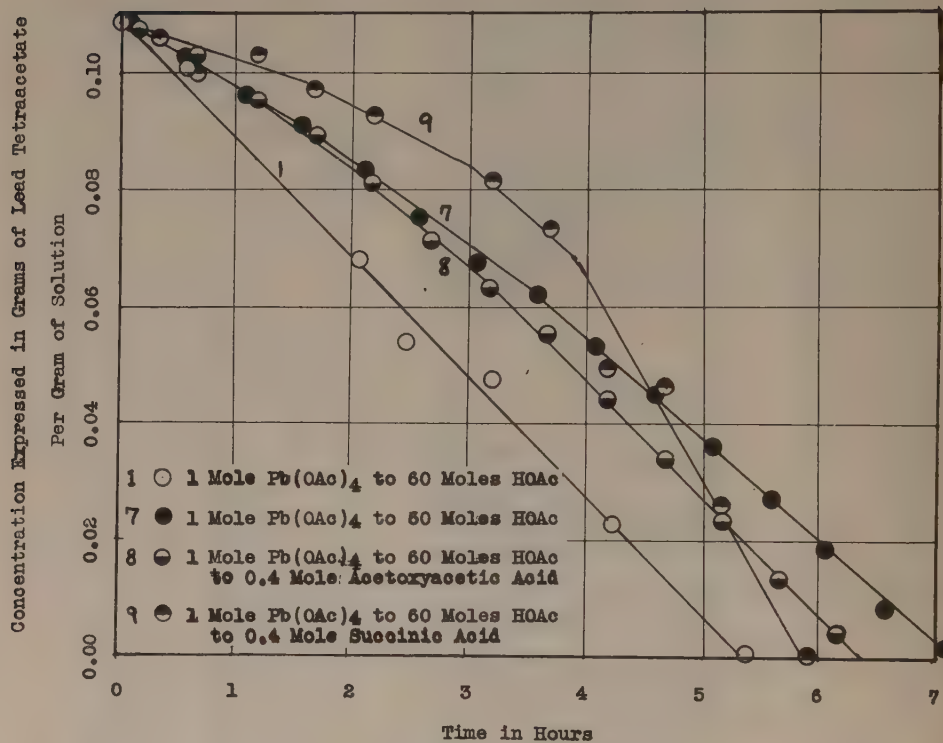
GRAPH 1b

## KINETICS OF THE REACTION OF LEAD TETRAACETATE WITH ACETIC ACID



GRAPH IIa

KINETICS OF THE REACTION OF LEAD TETRAACETATE WITH ACETIC ACID





GRAPH IIb

KINETICS OF THE REACTION OF LEAD TETRAACETATE WITH ACETIC ACID

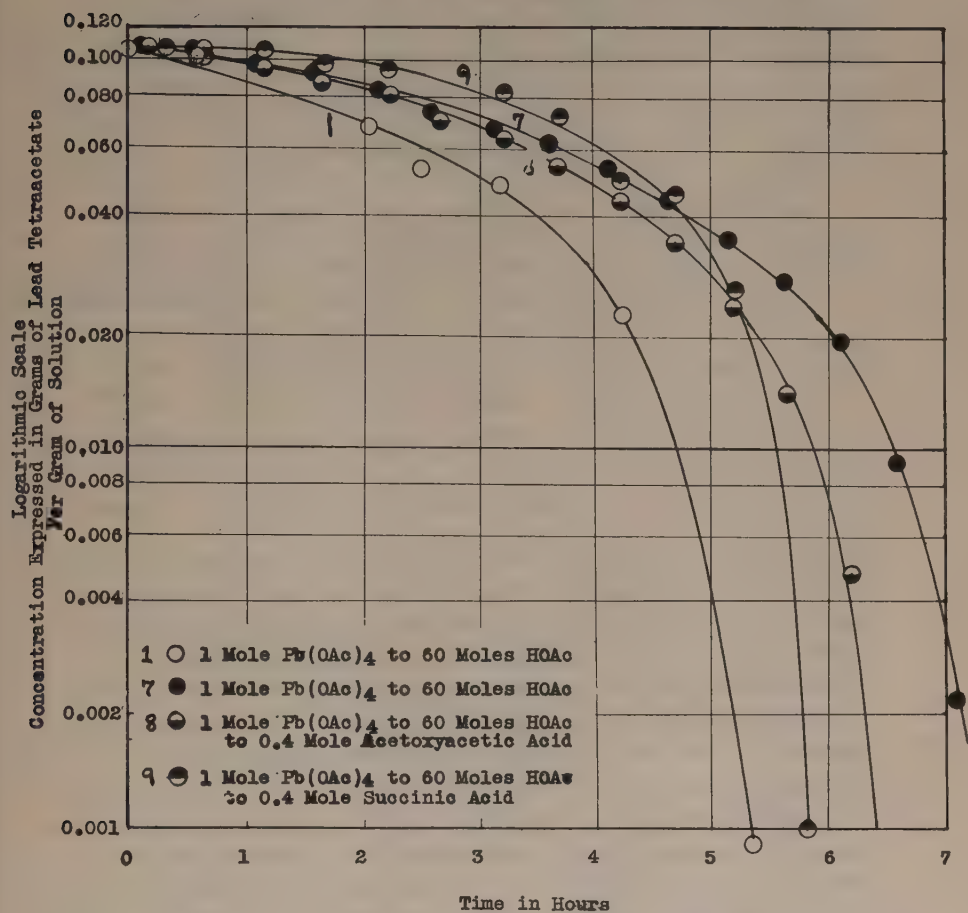


TABLE 6

EXPERIMENTAL CONDITIONS FOR KINETIC STUDIES OF LEAD TETRA-  
ACETATE DECOMPOSITIONS IN ACETIC ACID SOLUTIONS

| Run | Graph            | Time of Re-crystallization of $\text{Pb}(\text{OAc})_4$ | Moles of HOAc per Mole of $\text{Pb}(\text{OAc})_4$ | Added Reagents<br>0.4 Mole per Mole $\text{Pb}(\text{OAc})_4$ |
|-----|------------------|---------------------------------------------------------|-----------------------------------------------------|---------------------------------------------------------------|
| 1   | Ia, Ib, IIa, IIb | long                                                    | 60                                                  | none                                                          |
| 2   | Ia, Ib           | long                                                    | 30                                                  | none                                                          |
| 3   | Ia, Ib           | long                                                    | 60                                                  | acetoxyacetic acid                                            |
| 4   | Ia, Ib           | long                                                    | 60                                                  | methylene diacetate                                           |
| 5   | Ia, Ib           | long                                                    | 60                                                  | lead diacetate                                                |
| 6   | Ia, Ib           | long                                                    | 60                                                  | formic acid                                                   |
| 7   | IIa, IIb         | short                                                   | 60                                                  | none                                                          |
| 8   | IIa, IIb         | short                                                   | 60                                                  | acetoxyacetic acid                                            |
| 9   | IIa, IIb         | short                                                   | 60                                                  | succinic acid                                                 |

tetraacetate at a faster rate than with the acetic acid. This was verified by the addition of acetoxyacetic acid (0.4 mole, curves 3 and 8) and methylene diacetate (0.4 mole, curve 4). Acetoxyacetic acid and methylene diacetate are products of the decomposition of lead tetraacetate in acetic acid; 0.4 of a mole is the approximate concentration at which acetoxyacetic acid is isolated at the end of a reaction. These products when added made no radical change in the reaction rate but produced an increase in rate especially during the latter portion of the reaction. Comparison of curves 1 and 3 and curves 7 and 8 shows the same relationship between the curves on the addition of acetoxyacetic acid and those without, for the same batch of lead tetraacetate.

The addition of 0.4 mole of lead diacetate (curve 5) produced no change in reaction rate (compare curve 1). On the other hand the addition of 0.4 mole of formic acid (curve 6) produced a rapid increase in reaction rate at the beginning of the reaction. However, once the formic acid was used up, the normal slow reaction continued with a slower rate since the concentration of lead tetraacetate had been decreased by the initial rapid reaction. This behavior was in contrast to that of added acetoxyacetic acid (curves 3 and 8) and added methylene diacetate (curve 4) where the increase in rate occurred gradually being strongest near the end

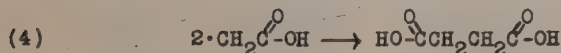
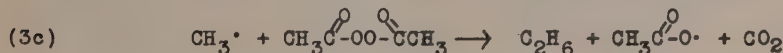
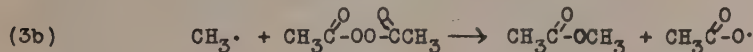
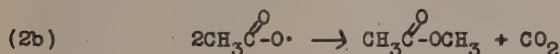
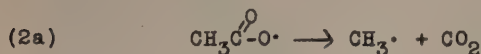
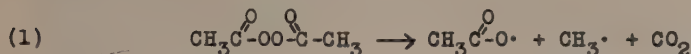
of the reaction.

The addition of 0.4 of a mole of succinic acid (curve 9) showed a decrease in the rate of the reaction at the beginning and a sharp increase at the end. This effect is different than that observed on the addition of acetoxyacetic acid.

## DISCUSSION SECTION

### The Reaction of Acetyl Peroxide with Acetic Acid

The reaction mechanism proposed for the reaction of acetyl peroxide with acetic acid<sup>29, 30</sup> is as follows:



Reaction (1) consists of the thermal decomposition of the acetyl peroxide. Reactions (3b) and (3c) are side reactions of a chain nature. This mechanism is supported by the results in Table 5, column 3.

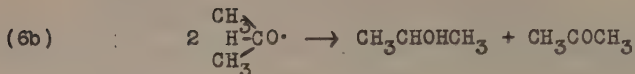
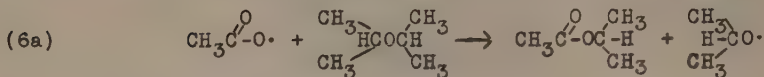
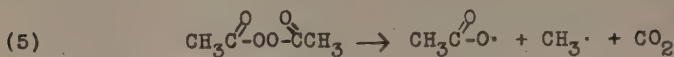
### The Reaction of Acetyl Peroxide with Isopropyl Ether

A similar scheme has been advanced for the reaction of

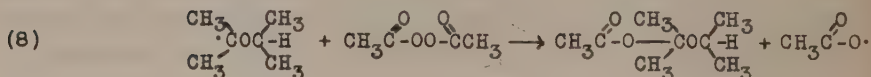
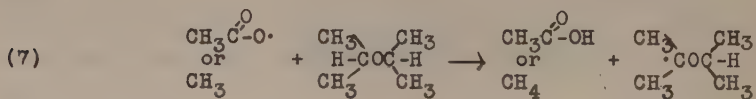
<sup>29</sup>Ibid.

<sup>30</sup>H. C. McBay, Ph.D. dissertation, Department of Chemistry, University of Chicago, 1945.

acetyl peroxide with isopropyl ether.<sup>31</sup>



The differences are that in this case there is evidence to show that the free acetoxyl radical has sufficient energy to react with the ether<sup>32</sup> (see reactions 6a and 6b). The data in Table 4, column 2, show the common origin of the acetone, isopropanol, and isopropyl acetate. Also in this case the fate of the radicals produced from the solvent (reaction 7) is unknown. There are two possible hypotheses as to their fate. (1) They disproportionate to form the corresponding unsaturated ether which polymerizes, accounting for the relatively large residue found. (2) There is the possibility of a chain reaction similar to that postulated by Cass<sup>33</sup> for the reaction of ethers with benzoyl peroxide. The chain reaction is illustrated by equations 7 and 8.



<sup>31</sup>Kharasch and Fineman, *op. cit.*

<sup>32</sup>For a complete discussion of the relative reactivities of methyl and acetoxyl free radicals, see J. L. Rowe, Ph.D. dissertation, Department of Chemistry, University of Chicago, 1946.

<sup>33</sup>Cass, *J. Am. Chem. Soc.*, **69**, 500 (1947).



The Reaction of Lead Tetraacetate with  
Isopropyl Ether

Both Fieser<sup>34</sup> and Waters<sup>35</sup> have considered that lead tetraacetate breaks down to form the same free radicals as are formed in the decompositions of acetyl peroxide. This hypothesis seems improbable on three grounds. First, the thermal decomposition of lead tetraacetate occurs at a temperature much higher than that generally used for lead tetraacetate decompositions in solvents. The thermal decomposition of acetyl peroxide on the other hand occurs at a much lower temperature and at the temperature generally used for acetyl peroxide decompositions in solution. Schall and Melzer<sup>36</sup> studied the thermal decomposition of lead tetraacetate at the anode during electrolysis of lead diacetate. The thermal decomposition of lead tetraacetate takes place only slowly at 140-80° and is not rapid until a temperature of about 213° is reached. The products are 62% CO<sub>2</sub>; 25-27% ethane; 4% methane; and traces of unsaturated hydrocarbons, carbon monoxide, and hydrogen. The thermal decomposition of acetyl peroxide takes place at 70° and is explosively violent at 90°. Second, the rate of reaction with lead tetraacetate varies greatly from solvent to solvent even among those of the same general type as was pointed out in the introduction, whereas the rate of decomposition of acetyl peroxide depends almost entirely on the temperature and only to a limited degree on the solvent. Third, if the same radicals were produced in both cases, the same products would be expected. This is not the case for many solvents since the reaction products of the reaction of acetyl peroxide and lead tetraacetate vary considerably. In particular, in the case for isopropyl ether and acetic acid, lead tetraacetate and acetyl peroxide give widely different products (compare the data given in Tables 4 and 5).

Despite the fact that lead tetraacetate does not break down in solution to give the same free radical fragments that acetyl peroxide does, there is ample evidence that many reactions

<sup>34</sup>Fieser and Chang, op. cit.; Fieser, Clapp, and Daudt, op. cit.; Fieser and Oxford, op. cit.

<sup>35</sup>Waters, op. cit.

<sup>36</sup>Schall and Melzer, Z. Elek. Chem., 2, 474, 506 (1938).

of lead tetraacetate proceed via free radical chain reactions. This evidence is of the following nature. In the decompositions of lead tetraacetate in certain solvents, especially at higher temperatures, methane and carbon dioxide are formed, although not in the amounts found in the reactions of acetyl peroxide. The methane is indicative of the presence in solution of free methyl radicals, and the carbon dioxide of the presence of free acetoxyl radicals.

The presence of a small proportion of free methyl radicals from the decomposition of lead tetraacetate in solution accounts for the methylation reactions observed by Fieser.<sup>37</sup> Thus, one mole of trinitrotoluene and five moles of lead tetraacetate gave three-tenths of a mole of trinitrometaxylene, whereas one mole of trinitrotoluene and one mole of acetyl peroxide yields three-tenths of a mole of trinitrometaxylene. The superiority of acetyl peroxide in the methylation reaction is thus quite obvious.

Lead tetraacetate catalyzes the auto-oxidation of tetralin to tetralin hydroperoxide<sup>38</sup> as do many other reagents which are known to produce free radicals in solution. Lead tetraacetate and benzenediazoacetate<sup>39</sup> give the same product on the oxidation of cyclohexene, namely cyclohexene-3-acetate. Benzenediazoacetate is known to decompose in solution to produce nitrogen gas, and phenyl and acetoxyl free radicals.

Bell, Sturrock, and Whitehead,<sup>40</sup> investigating the kinetics of the reaction between ethylene glycol and lead tetraacetate in acetic acid solution, found the reaction to be first order in both reactants and to fit the following Arrhenius equation:

$$k_2 = 1.95 \times 10^{14} e^{-20900/RT}$$

The collision factor is so close to that for a simple collision and since the reaction is between two uncharged molecules, Bell, Sturrock, and Whitehead concluded that a free radical mechanism

<sup>37</sup>Fieser and Chang, op. cit.; Fieser, Clapp, and Daudt, op. cit.; Fieser and Oxford, op. cit.

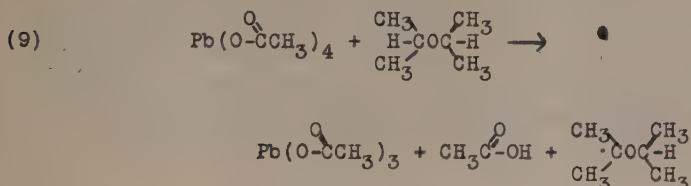
<sup>38</sup>Robertson and Waters, Trans. Farad. Soc., **42**, 201 (1946).

<sup>39</sup>Waters, J. Chem. Soc., 1939, 1805.

<sup>40</sup>Bell, Sturrock, and Whitehead, J. Chem. Soc., 1940, 82.

is indicated.

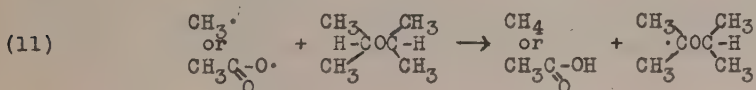
In my estimation the following scheme for the reaction of lead tetraacetate with isopropyl ether is superior to the hypotheses cited above, and accounts for the reaction products (see Table 4, column 1). The first step (reaction 9)

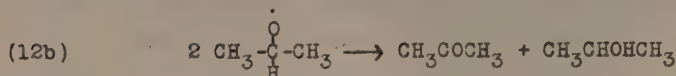
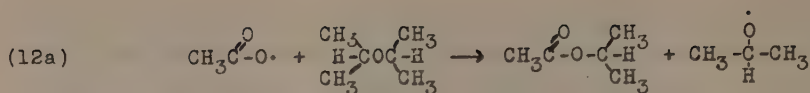


is a bimolecular reaction between lead tetraacetate and the solvent molecule containing a reactive hydrogen atom. This scheme accounts for the great differences in the reaction rates observed in the decomposition of lead tetraacetate in different solvents. The rate of the reaction would depend on the energy available in the activated complex for removal of the hydrogen atom. The second step deals with the decomposition of free lead triacetate radicals and may be formulated as follows:

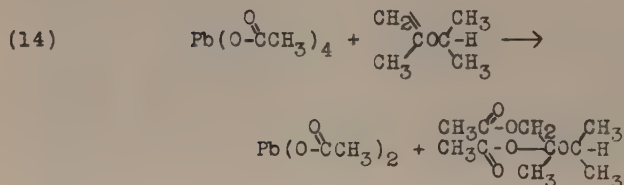
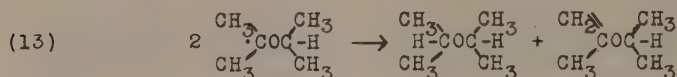


Reaction 10a is to be considered as the more common reaction especially at lower temperatures. At higher temperatures, Reactions 10b and 10c increase in importance and more free radicals are produced. Step three (reactions 11, 12a, and 12b; compare reactions 6a, 6b, and 7) deals with the reactions of the free radicals formed in step two.



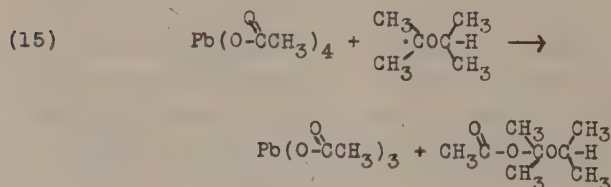


The free radicals formed in equations 9 and 11 presumably disproportionate as indicated in equation 13, and the unsaturated compound thus formed reacts further with lead tetraacetate as indicated schematically in equation 14.



Since some tarry residue is found, polymerization and further attack of some of the solvent radical products must occur.

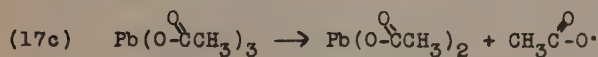
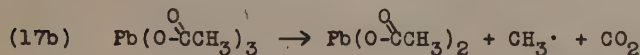
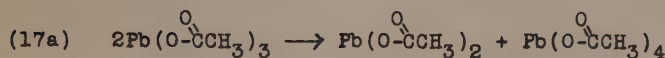
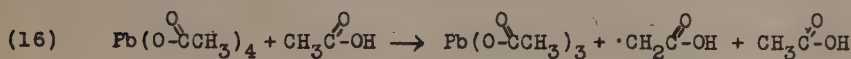
A chain reaction of the type postulated for the acetyl peroxide reaction (see reactions 7 and 8) might be applicable for the lead tetraacetate reaction. The scheme would be as follows, either reactions 9 or 11 followed by reaction 15.



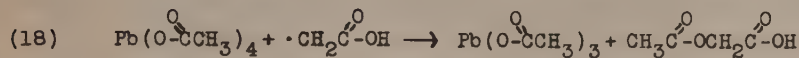
No esters of this type were isolated. Furthermore, it does not seem likely that on further attack of the 2-acetoxyisopropyl ether, the 1,2-diacetoxyisopropyl ether found would be formed exclusively. Mixtures of diacetoxyisopropyl ethers would be expected.

The Reaction of Lead Tetraacetate with Acetic Acid

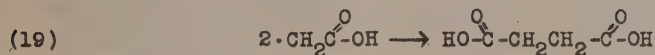
A similar scheme (reactions 16 and 17, compare 9 and 10)



explains the reaction of acetic acid and lead tetraacetate. To explain the non-formation of succinic acid in the reaction of lead tetraacetate and acetic acid, we must assume that reaction 18 predominates



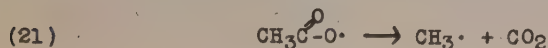
and does not allow the dimerization reaction to take place (reaction 19--the formation of succinic acid).



The methyl radicals produced react with the solvent in the same manner as in the acetyl peroxide reaction (reaction 20, compare reaction 3)

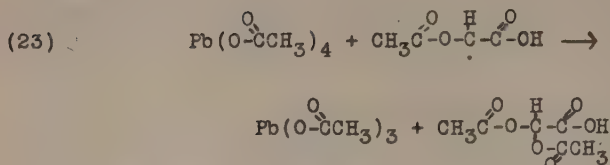
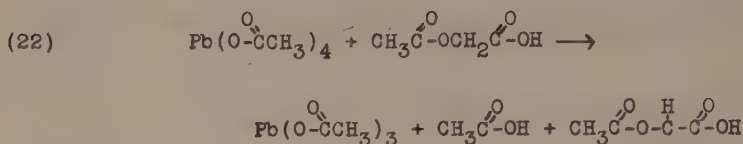


producing more solvent free radicals which then react with the lead tetraacetate (reaction 18). Since the few acetoxyl radicals formed cannot attack the solvent, they break down to form methyl radicals and carbon dioxide (reaction 21).

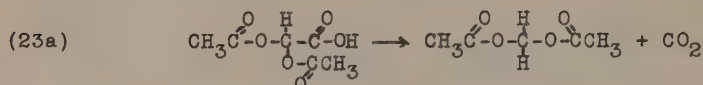




Although the concentration of acetoxyacetic acid is low, the secondary hydrogen atoms which it contains make it liable to further attack by lead tetraacetate (reactions 22 and 23).



The diacetoxyacetic acid formed can lose carbon dioxide (reaction 23a)



at the temperature of the reaction to form methylene diacetate which is found as a reaction product. This scheme accounts for the amount of carbon dioxide in excess of methane formed in the reaction. This hypothesis is supported by the fact that the proportion of methylene diacetate and the amount of carbon dioxide in excess of the amount of methane is greater in the experiment in which acetoxyacetic acid was added, Table 5, column 5.

The relatively greater ease of attack on acetoxyacetic acid compared to acetic acid is also shown by the lower reaction temperature and greater speed of the reaction in the run where a large amount of added acetoxyacetic acid is present.

Apparently both the methylene diacetate and diacetoxyacetic acid are attacked further in the same manner, or the products of their attack are very rapidly attacked. This is to be expected since these two substances have very reactive hydrogen atoms. This hypothesis is supported by the kinetic studies made. As the amount of these secondary products build up the rate of decomposition of lead tetraacetate increases. When either acetoxyacetic acid or methylene diacetate were added this increase in reaction

rate was made more rapid (compare the graphs previously given). Since the increase in rate was not immediate, we must conclude that the acetoxyacetic acid and the methylene diacetate are not the products which react rapidly with lead tetraacetate but rather, they are the precursors of these products. The fact that acetoxyacetic acid is somewhat more effective in producing this increase than the same amount of methylene diacetate, suggests that the diacetoxyacetic acid can react before decarboxylation to form methylene diacetate. Since no products of the further attack of methylene diacetate and diacetoxyacetic acid are found, we must conclude that, either the molecules break down to form acetic acid and carbon dioxide, or that aldehydic materials result which polymerize and form the tarry residue. The amount of carbon dioxide in excess of methane would be expected to equal the amount of methylene diacetate formed. However, this is not the case. The amount of methylene diacetate found is always too small. A further attack on the methylene diacetate accounts for this discrepancy.

The non-reproducibility found in the kinetic studies and mentioned in the section "A Study of the Kinetics of the Reaction between Lead Tetraacetate and Acetic Acid" on page 21 also support the theory that the products of the attack on acetic acid by lead tetraacetate react further since the length of time during which the lead tetraacetate is in contact with the hot acetic acid during recrystallization will determine the amount of impurities, such as lead tetraacetoxyacetate, that are capable of increasing the reaction rate. This non-reproducibility in the kinetic studies is also reflected in the differences in the products obtained in the two runs shown in Table 5, columns 1 and 2. The lead tetraacetate used in the run described in column 2 was of shorter recrystallization time. The reaction took longer to go to completion, although it was run at a higher temperature. More acetoxyacetic acid was found and less methylene diacetate, showing a smaller proportion of attack on daughter products.

In the mixed decomposition of lead tetraacetate and acetyl peroxide (see Table 5, column 4) very little of the primary products, acetoxyacetic acid and succinic acid, are found. Apparently in the presence of the large amount of free methyl radicals these primary products suffer further attack. The large excess of carbon dioxide over methane is a further indication of this attack.

That a larger amount of succinic acid than acetoxyacetic acid is found in this reaction mixture is probably due to the large local concentrations of solvent free radicals in the drops of acetyl peroxide solution as they are added to the lead tetraacetate solution; and, to the fact that some acetyl peroxide may be added after all the lead tetraacetate has reacted.

Proposed Mechanism for the Reaction of Lead  
Tetraacetate with Organic Compounds

Lead tetraacetate is a versatile reagent in that it undergoes different types of reactions with different organic molecules and that it reacts with so many organic compounds. Lead tetraacetate is unique in undergoing at lower temperatures ionic reactions with glycols and alcohols and at higher temperatures free radical reactions with other types of compounds.

Waters<sup>41</sup> (see section "Proposed Mechanisms of the Reactions of Lead Tetraacetate" on page 15) postulates that in the oxidation of glycols the first step in the reaction is the breakdown of lead tetraacetate to form free acetoxyl and free methyl radicals. These free radicals are the same as those postulated to be the active agents in the decomposition reactions of acetyl peroxide. Waters therefore states that lead tetraacetate and acetyl peroxide should give the same products on reaction with organic molecules. We have found this not to be the case for the reactions of lead tetraacetate and acetyl peroxide with acetic acid and isopropyl ether. Furthermore, preliminary studies have shown that glycols are not cleaved by acetyl peroxide. The latter reagent oxidizes glycols to the corresponding hydroxy ketones and diketones.

Another difference between lead tetraacetate and acetyl peroxide is the point of attack on glycols and alcohols. Acetyl peroxide attacks the hydrogen atoms attached to the carbon atom holding the hydroxyl group whereas lead tetraacetate attacks the hydrogen atoms attached to the oxygen atoms. Thus preliminary studies have shown that acetyl peroxide attacks secondary glycols, like hydrobenzoin, with more ease than tertiary glycols, like pinacol, whereas lead tetraacetate attacks either with equal ease. Furthermore, acetyl peroxide attacks isopropyl alcohol with

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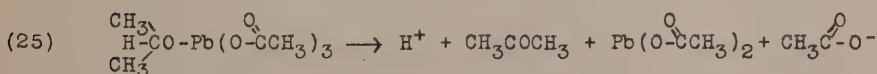
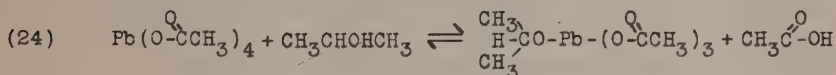
<sup>41</sup>Waters, J. Chem. Soc., 1946, 409; Trans. Farad. Soc., 42, 184 (1946).

greater ease than tertiary butyl alcohol.<sup>42</sup> In the cases of isopropyl alcohol and tertiary butyl alcohol deuterium tracer experiments have shown that the hydrogen atom attached to the oxygen atom is not attacked by acetyl peroxide.<sup>43</sup>

No methane or carbon dioxide is formed during the reactions of lead tetraacetate with glycols and alcohols. Methane and carbon dioxide would be expected if either free methyl or free acetoxyl radicals existed in solution during the reaction.

Because of this evidence, Waters' hypothesis is untenable. The mechanism postulated by Criegee<sup>44</sup> and discussed in the section, "Proposed Mechanisms of the Reactions of Lead Tetraacetate," is satisfactory for the reaction of lead tetraacetate and glycols with the reservation that it seems more likely that the cyclic intermediate postulated in reaction 26 (page 16) breaks into three fragments rather than two. That is the 1,4-diradical which Criegee has postulated could have only momentary existence. This mechanism accounts for the rapidity of the reaction, the ease in cleaving a carbon to carbon bond, the specificity for free hydroxyl groups, and the faster rate of reaction of a cis glycol compared to a corresponding trans glycol.

The dehydrogenation of alcohols (see Table 1), like the glycol cleavage reaction, occurs at low temperatures and is nearly quantitative. Furthermore, no methane or carbon dioxide is formed in this reaction. A mechanism similar to that which Criegee advanced for the glycol cleavage reaction is appropriate. The initial reaction is the ionic replacement of an alkoxyl group for an acetoxyl group on the lead atom. The new lead salt then undergoes fission into four fragments, aided by the removal of the hydrogen ion by a basic material in solution such as acetate ion.




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<sup>42</sup>Kharasch, Rowe, Urry, and Friedlander, Unpublished results.

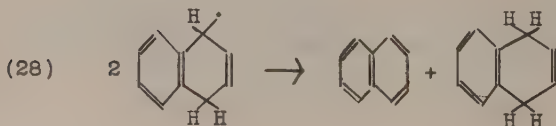
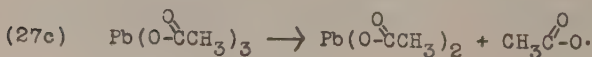
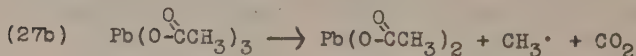
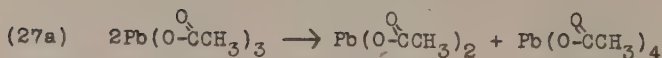
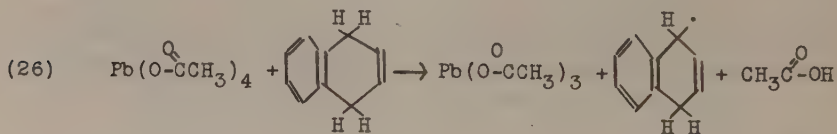
<sup>43</sup>Ibid.

<sup>44</sup>Criegee, Kraft, and Rank, op. cit.

In reactions of lead tetraacetate at higher temperatures (dehydrogenation of hydrocarbons, acetoxylation) there is evidence of the existence of free radicals. Methane and carbon dioxide are usually found, although not in high yields. The formation of these gases indicates the existence of free radicals in solution. However, Waters' hypothesis for their formation by the thermal breakdown of lead tetraacetate is still untenable. The reasons for this are threefold (as discussed in the section on page 29).

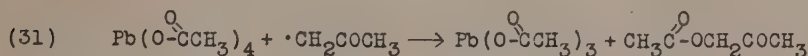
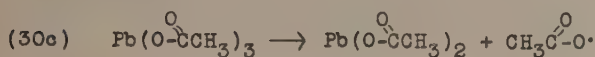
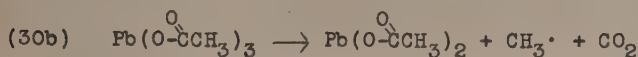
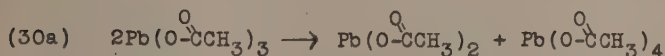
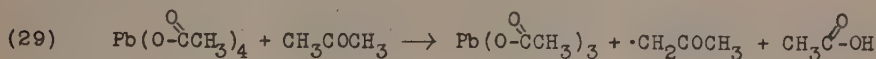
(1) The thermal decomposition of lead tetraacetate occurs at temperatures higher than those used in these reactions. (2) The rate of reactions varies greatly from compound to compound. (3) Lead tetraacetate and acetyl peroxide reacting with the same compound give different products. On the other hand the reaction scheme here postulated assumes a bimolecular reaction of the lead tetraacetate and the compound containing the reactive hydrogen atom and the consequent formation of a lead triacetate free radical. The free lead triacetate radical can either disproportionate to lead tetraacetate and lead diacetate or decompose to form free acetoxy radicals or free methyl radicals and carbon dioxide.

The scheme for the dehydrogenation of hydrocarbons is identical with that postulated for isopropyl ether (reactions 9, 10, and 13 on pages 31 and 32) and is illustrated in the case of 1,4-dihydronaphthalene.



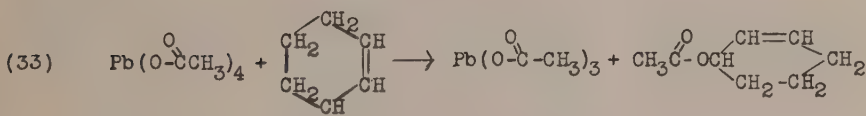
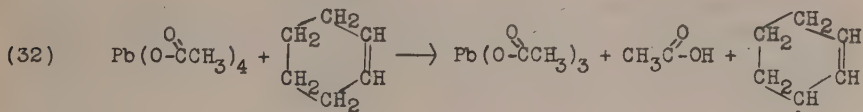


The scheme for the acetoxylation reaction is identical with that postulated for acetic acid (reactions 16, 17, and 18 on page 33) and is illustrated in the case of acetone.

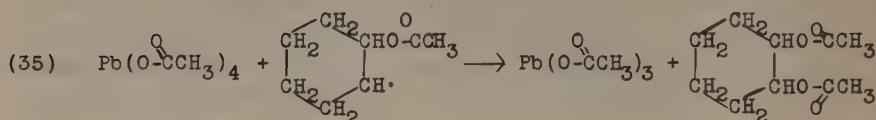
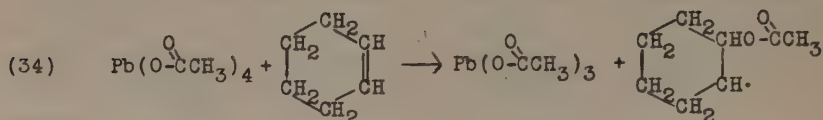


The reaction scheme postulated in equations 26-28 or 29-31 explains the difference in reaction rates between various compounds. Since the first step (equations 26 or 29) would be expected to be rate determining, the rate of the reaction depends on the energy available to remove the hydrogen atom in the activated complex formed during the first step. This scheme also explains the low yields found from the reaction (see Tables 1, 2A and 2B), since the breakdown of lead triacetate to free radicals is a side reaction which uses up lead tetraacetate.

The reaction with olefins can take two courses. The first is entirely analogous to the acetoxylation reaction just discussed. The acetoxylation of cyclohexene can be postulated as follows.



The second course of reaction possible is addition of two acetoxyl groups.



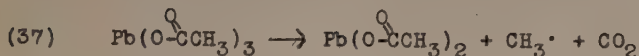
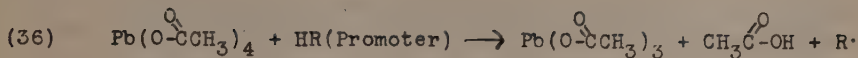
The lead triacetate undergoes the same reactions as were indicated before (reactions 27 and 30).

The methylation reactions of Fieser<sup>45</sup> depend on the production of methyl radicals from the lead triacetate fragment as previously indicated (reaction 27). The promoters used by Fieser facilitated the production of lead triacetate which in turn produced methyl radicals by reaction 27b. In the absence of added promoters, a higher temperature was necessary to affect the methylation since acetic acid is only slowly attacked by lead tetraacetate to give lead triacetate. Acetic acid thus acted as a promoter. In some cases the compound to be methylated itself acted as a promoter. The need for a large excess of lead tetraacetate is explained since the promoter used up the lead tetraacetate forming only a relatively small proportion of methyl radicals, whereas acetyl peroxide, giving a large proportion of methyl radicals was not needed in excess. Since the reaction depends on the production of methyl radicals, both lead tetraacetate and acetyl peroxide (and any other material which will produce methyl radicals in solution) will give the reaction. Thus, acetyl peroxide is more efficient as a producer of methyl radicals than lead tetraacetate and less acetyl peroxide is needed to obtain the same yield of the methylated product.

The general reaction is illustrated in the case of tri-nitrotoluene.

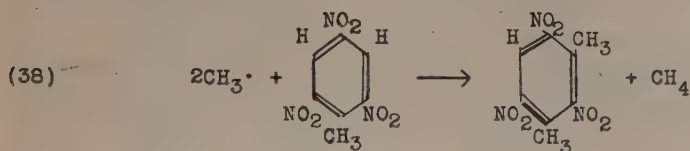
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<sup>45</sup>Fieser and Chang, op. cit.; Fieser, Clapp, and Daudt, op. cit.; Fieser and Oxford, op. cit.



That the methyl radicals come from the lead tetraacetate was shown in equation 23 on page 14.

Reaction 37 is followed by the methylation of the aromatic ring by the methyl radical. The exact nature of the addition of methyl radicals to the aromatic ring is as yet unknown. Reaction 38 is schematic.



## EXPERIMENTAL PART

### Reagents

Lead tetraacetate.--Lead tetraacetate for the isopropyl ether experiments was prepared by the method described by Fieser<sup>46</sup> (procedure two). However, this method gave a product which contained 10% lead chloride. This material, in the first experiments performed in acetic acid, gave methyl chloride. For that reason, in all further experiments performed in acetic acid and in the kinetic studies, the lead tetraacetate was prepared by procedure one described by Fieser.<sup>47</sup> The lead tetraacetate was stored in a vacuum desiccator with no drying agent. It was analyzed by the following procedure. To a warm solution of lead tetraacetate in glacial acetic acid was added 10 cc. of a potassium iodide stock solution made up as follows: 150 gm. KI, 250 gm. sodium acetate (to buffer the solution), and 100 gm. of sodium carbonate (to produce carbon dioxide to displace air from the flask) made up to

<sup>46</sup>L. F. Fieser, "Experiments in Organic Chemistry," 2d ed., D. C. Heath and Co., New York, 1941, p. 437.

<sup>47</sup>Ibid., p. 436.

1 liter of solution in water. After heating for one minute on a steam bath, the liberated iodine was titrated by 0.1 N thiosulfate.<sup>48</sup> Lead tetraacetate prepared by procedure two was found to be 90% lead tetraacetate whereas that from procedure one was 100% lead tetraacetate.

Isopropyl ether.--Eastman's practical grade isopropyl ether was washed three times with saturated potassium permanganate solution, and distilled through a 30-plate column. Until it was used it was stored in a brown glass bottle over sodium wire.

Acetic acid.--Purified as described by Kharasch and Hobbs.<sup>49</sup>

Acetoxyacetic acid.--Prepared from sodium acetate and chloroacetic acid, and recrystallized from benzene. The melting point of the material used in the experiments was 67-68°.

Methylene diacetate.--Prepared according to the procedure described by Knoevenagel:<sup>50</sup>  $n_D^{20} = 1.4048$ ; b.p. 82° (32mm.).

Anhydrous lead diacetate.--Prepared by drying lead diacetate trihydrate at reduced pressure until constant weight at 75°C; m.p. 180°C.

Formic acid.--A small quantity of anhydrous formic acid was prepared by fractional crystallization according to Ewins.<sup>51</sup>

Acetyl peroxide.--Acetyl peroxide was made in 15 gram batches by the dropwise addition of 40 grams of acetic anhydride to a slurry of 46 grams of barium peroxide in 100 cc. of water and 100 cc. of ether. The temperature was kept below 10°C. The ether layer was separated and dried with  $\text{CaCl}_2$ . On subsequent freezing to -80° in dry ice, the acetyl peroxide crystallized and was separated by decantation of the ether and removal of the last traces of solvent at low temperatures (0°) and low pressures. Analysis of the diacetyl peroxide by the method of Kokatnur and Jelling<sup>52</sup> showed it to be 98% diacetyl peroxide.

<sup>48</sup> Modification of method of Hackett and McClenahan, J. Am. Chem. Soc., **61**, 1670 (1939).

<sup>49</sup> Kharasch and Hobbs, J. Org. Chem., **6**, 708 (1941).

<sup>50</sup> Knoevenagel, Ann., **402**, 127 (1914).

<sup>51</sup> Ewins, J. Chem. Soc., **105**, 350 (1914).

<sup>52</sup> Kokatnur and Jelling, J. Am. Chem. Soc., **63**, 1432 (1941).

Reaction of Lead Tetraacetate with  
Isopropyl Ether

Lead tetraacetate (342 grams, .771 moles) was placed in a 3-liter, three-necked flask fitted with a mercury sealed stirrer and a condenser. Isopropyl ether (1021 grams, 10 moles) was poured over it, and the mixture was heated to reflux with constant stirring. The evolved gases were led from the condenser through a trap immersed in a  $-80^{\circ}$  bath into weighed U-tubes, the first two containing soda lime, and the last containing Ascarite, and finally collected over water in a gas collector. As the reaction started, the mixture became light yellow in color, and after a period of from 8 to 10 hours, the solution became colorless and gas evolution ceased.

The soda lime and Ascarite absorption tubes had absorbed 0.125 moles of carbon dioxide. The gas in the gas collector was methane (0.124 moles: molecular weight, calculated 16.0, found 16.1). The reaction mixture was filtered to remove precipitated lead acetate, and the filtrate was distilled through a 100-plate Podbielniak HeliGrid column. An azeotropic mixture containing acetone, isopropanol, and isopropyl ether distilled first. The acetone content (0.0031 moles) was determined according to the method of Perkins and Edwards<sup>53</sup> which employs quantitative precipitation and weighing of the 2,4-dinitrophenylhydrazone (m.p.  $124.5-125^{\circ}$ ). The isopropanol (0.0035 moles) was determined by the method of Freed and Wynn<sup>54</sup> and the phenylurethane (m.p.  $87-87.5^{\circ}$ ) was made.

After the isopropyl ether had been removed, the higher boiling residue was subjected to vacuum distillation through a 10-plate column packed with concentric tubes. This distillation separated the solution into an azeotrope of isopropyl acetate and acetic acid, pure acetic acid, and a high boiling ester. The amount of acetic acid in the azeotrope was determined by titration. The total amount of acetic acid was 1.045 moles. The p-bromophenacyl ester was made (m.p.  $124-125^{\circ}$ ). Isopropyl acetate (0.0092 moles) was determined by saponification.

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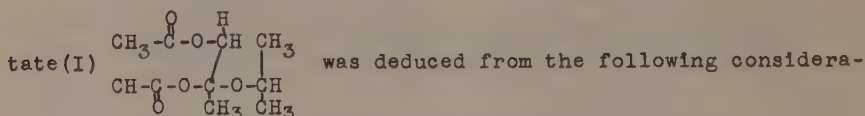
<sup>53</sup>Perkins and Edwards, Am. J. of Pharmacy, 107, 206 (1935).

<sup>54</sup>Freed and Wynn, Ind. and Eng. Chem., Anal. Ed., 8, 278 (1936).



### Identification of the High Boiling Ester

The structure of the ester, a heavy oil of light yellow color, as 1-methyl-1-isopropoxy-ethylene-glycol-diacetate(I)



tions. Derivatives of each of the fragments of the molecule following saponification were obtained. From the hydroxyacetone fragment, a 2,4-dinitrophenylosazone was prepared which melted at  $298^\circ(\text{cor})$ . Analysis calculated for  $\text{C}_{15}\text{H}_{12}\text{O}_8\text{N}_8$ : N, 25.93. Found: N, 25.22. The compound failed to depress the melting point of a known sample of the osazone (m.p.  $298^\circ$ ).<sup>55</sup> From the acetic acid portion, the p-bromophenacyl ester was prepared (m.p.  $123.5\text{--}125^\circ$ ). From the isopropanol portion, the phenylurethane was prepared (m.p.  $88\text{--}88.5^\circ$  uncor.).

The molecular weight was determined in benzene solution and found to be 217 (calculated for I, 218.2). Saponification equivalent in  $\text{Ba}(\text{OH})_2$ : found, 105; calculated for I, 109.1. Analysis: calculated for  $\text{C}_{10}\text{H}_{18}\text{O}_5(\text{I})$ : C, 55.03; H, 8.29. Found: C, 53.47; H, 7.61. The refractive index is  $n_D^{20} = 1.4386$ .

### The Reaction of Lead Tetraacetate with Acetic Acid

In an apparatus similar to that used for the isopropyl ether runs were placed acetic acid (435 grams, 7.25 moles) and lead tetraacetate (227 grams, 0.512 moles). With constant stirring the solution was heated to  $120^\circ$ , the boiling point. As the reaction started, the mixture became light yellow in color, and after 12-14 hours became dark brown and gas evolution ceased. The soda lime and Ascarite absorption tubes absorbed 9.45 grams or 0.215 moles of carbon dioxide. The gas in the gas collector was methane 0.156 moles. The clear reaction mixture was then dropped with rapid stirring into three liters of anhydrous ether precipitating in a gummy mass the lead salts of acetic and acetoxyacetic acids. The ether solution was decanted and the ether and acetic acid were removed by distillation through a 30-plate glass

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<sup>55</sup>Bulow and Seidel, Ann., 439, 55 (1924).

helix column. The methylene diacetate (0.03 moles) was then distilled from the mixture at  $82^{\circ}$  (32mm.) and checked by quantitative analysis for formaldehyde<sup>56</sup> produced from  $\text{Ba}(\text{OH})_2$  hydrolysis. The methone derivative for formaldehyde was obtained (m.p.  $189-90^{\circ}\text{C}$ , literature  $189^{\circ}\text{C}$ ). The remaining solids were treated with hot benzene obtaining part of the acetoxyacetic acid (m.p.  $67-68^{\circ}$  does not depress the melting point of authentic samples of acetoxyacetic acid) from the soluble portion, and a trace of succinic acid forming the insoluble portion. The gummy mass of lead salts was dissolved in glacial acetic acid and the lead was precipitated as lead chloride by dry gaseous  $\text{HCl}$ . The filtered acetic acid solution was subject to distillation, removing the acetic acid and leaving a residue which when treated with hot benzene yielded the remainder of the acetoxyacetic acid giving a total of 0.202 moles. The acetoxyacetic acid was further identified by conversion into the amide of glycolic acid (m.p.  $116-7^{\circ}$ , literature  $118.5-119.5^{\circ}$ ).

#### The Reaction of Lead Tetraacetate and Acetyl Peroxide with Acetic Acid

For the reaction of acetyl peroxide in acetic acid in the presence of lead tetraacetate the following modification of the above procedure was used. The acetyl peroxide dissolved in acetic acid was added dropwise below the surface of a solution of lead tetraacetate in acetic acid held at  $90^{\circ}$ . For quantitative data see Table 5, column 4. The succinic acid obtained melted at  $184-6^{\circ}$  (literature  $186-8^{\circ}$ ) and did not depress the melting point of authentic samples of succinic acid.

#### The Rate of Reaction of Lead Tetraacetate with Acetic Acid

The kinetic studies were run in a cylindrical vessel about 20 cm. long and 6 cm. in diameter fitted with a Tru-bore stirrer, a capillary tube leading from below the liquid level, and a condenser leading to a eudiometer.

The appropriate solutions were placed in the vessel and then the lead tetraacetate was added. The solution was then rapidly heated to the reflux point ( $120^{\circ}$ ) in an oil bath whose

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<sup>56</sup>Weinberger, Ind. Eng. Chem., Anal. Ed., **3**, 365 (1931).

temperature was controlled by a variac operating from a Sola constant voltage transformer.

The samples for titration were withdrawn from the capillary and weighed into weighed flasks, then analyzed in the same manner as samples of pure lead tetraacetate (see section, "Reagents"). The rate of gas evolution as measured in the eudiometer roughly paralleled the rate of decomposition of the lead tetraacetate.

### SUMMARY AND CONCLUSIONS

1. The reaction of lead tetraacetate with isopropyl ether gave lead diacetate, carbon dioxide, methane, acetic acid, diacetoxyisopropyl ether, and traces of acetone, isopropanol, and isopropyl acetate. The decomposition of acetyl peroxide in isopropyl ether gave carbon dioxide, methane, acetic acid, and appreciable quantities of acetone, isopropanol, and isopropyl acetate.

2. The reaction of lead tetraacetate with acetic acid gave lead diacetate, carbon dioxide, methane, acetoxyacetic acid, and a small quantity of methylene diacetate. The decomposition of acetyl peroxide in acetic acid gave carbon dioxide, methane, methyl acetate, and succinic acid.

3. A mechanism for the reaction of lead tetraacetate with isopropyl ether and acetic acid has been postulated. This mechanism involves the bimolecular free radical oxidation of the solvent by the lead tetraacetate producing free lead triacetate radicals and solvent free radicals. The free lead triacetate radicals can either disproportionate or decompose to give free acetoxy radicals or free methyl radicals and carbon dioxide. The solvent free radicals can either disproportionate, dimerize, or react with lead tetraacetate.

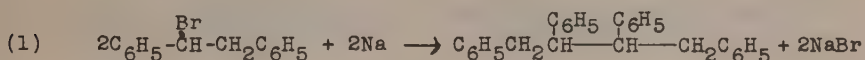
4. For the glycol cleavage reaction and the oxidation of alcohols by lead tetraacetate an ionic mechanism has been postulated. For the dehydrogenation of hydrocarbons, the acetoxylation reaction, and the methylation reaction of lead tetraacetate a free radical mechanism has been postulated. This mechanism is similar to that postulated for the reactions of lead tetraacetate with isopropyl ether and acetic acid. It is shown that these mechanisms are compatible with all the reactions of lead tetraacetate.

## PART II. RETENTION OF OPTICAL ACTIVITY BY FREE RADICALS

### INTRODUCTION

An approximate quantum mechanical demonstration due to Hückel<sup>1</sup> has demonstrated that a carbon atom attached to three atoms and carrying a single odd electron is most stable when the structure lies in a plane. This is certainly true for the free methyl radical, but may not be strictly true where the three groups attached to the carbon atom are not all the same. Specifically, Kharasch, Engelmann, and Urry<sup>2</sup> have demonstrated that the free 1-apocamphyl radical can exist. This radical cannot be coplanar, showing that it is not necessary to have coplanarity in order to have free radicals.

In the chapter on stereoisomerism in Gilman,<sup>3</sup> there is an excellent review of the optical activity of free radicals. In nearly all the cases where free radicals were produced at optically active centers, all activity was lost. Of note is the fact that Wallis and Adams<sup>4</sup> obtained inactive 1,2,3,4-tetraphenylbutane from the action of sodium on levo- $\alpha$ -bromobiphenyl (equation 1).



However, their result may be invalid since they isolated only one of the two possible forms, the meso and racemic. The inactive

<sup>1</sup>Hückel, Z. Elektrochem., 43, 752, 827 (1927); Cf. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, p. 16.

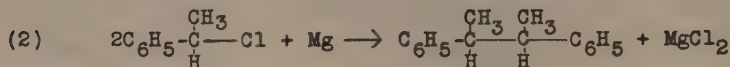
<sup>2</sup>Kharasch, Engelmann, and Urry, J. Am. Chem. Soc., 65, 2428 (1945).

<sup>3</sup>R. L. Shriner, R. Adams, and C. S. Marvel, chap. iv, "Stereoisomerism," H. Gilman (ed.), Organic Chemistry, I (2d ed.; New York: John Wiley and Sons, 1943), 383-88.

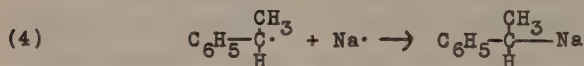
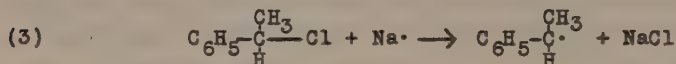
<sup>4</sup>Wallis and Adams, J. Am. Chem. Soc., 55, 3838 (1933).

material isolated by them could have been the meso form.

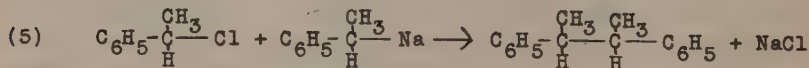
In a very interesting study, Ott and Behr<sup>5</sup> obtained inactive 2,3-diphenylbutane by the action of magnesium on optically active  $\alpha$ -chloroethylbenzene



whereas they obtained an active dimer by the action of sodium. Table 1 gives a résumé of their work. Shriner and Adams in the chapter on stereoisomerism in Gilman<sup>6</sup> explain this result by assuming that a sodium atom reacts with the free radical produced from the reaction of a halide molecule with sodium (equations 3 and 4).



The resulting sodium alkyl then reacts with optically active halide producing an optically active dimer (equation 5).



Brown, Kharasch, and Chao,<sup>7</sup> by the photochemical or peroxide catalyzed chlorination of d(+)-1-chloro-2-methylbutane obtained 1,2-dichloro-2-methylbutane, which had a residual activity of +0.05° to +0.22° which they ascribed to the small quantity of active 1,1-dichloro-2-methylbutane isomer also formed in the reaction. Equations 6, 7, and 8 show the chain reaction of which

<sup>5</sup>Ott, Ber., 61, 2124 (1928); Ott and Behr, Ber., 61, 2139 (1928).

<sup>6</sup>Shriner, Adams, and Marvel, op. cit., p. 386.

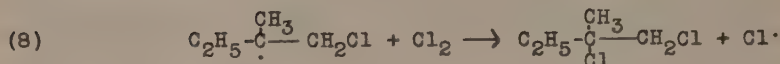
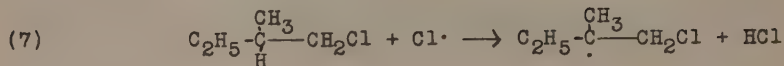
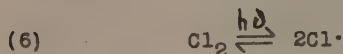
<sup>7</sup>Brown, Kharasch, and Chao, J. Am. Chem. Soc., 62, 3435 (1940).



TABLE 1

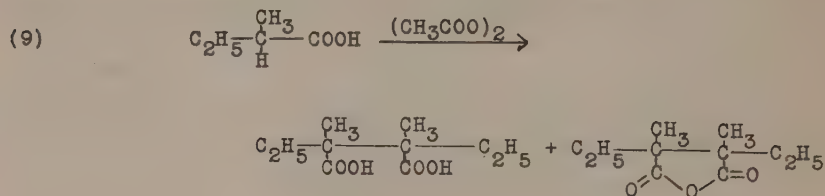
|                                         | Reaction |              |     |              |           |              |     |              |     |              |     |              |
|-----------------------------------------|----------|--------------|-----|--------------|-----------|--------------|-----|--------------|-----|--------------|-----|--------------|
|                                         | 1        |              | 1a  |              | 2         |              | 3   |              | 3a  |              | 3b  |              |
|                                         | Gm.      | $[\alpha]_D$ | Gm. | $[\alpha]_D$ | Gm.       | $[\alpha]_D$ | Gm. | $[\alpha]_D$ | Gm. | $[\alpha]_D$ | Gm. | $[\alpha]_D$ |
|                                         |          |              |     |              |           |              |     |              |     |              |     |              |
| Reactants                               |          |              |     |              |           |              |     |              |     |              |     |              |
| $\alpha$ -chloro-ethylbenzene           | 14       | 0°           | 16  | 6.81°        | 6         | 10.67°       | 14  | 0°           | 9   | +29.6°       | 9.8 | -50.27°      |
| Reagent                                 | Mg       |              | Mg  |              | Active Mg |              | Na  |              | Na  |              | Na  |              |
| Products                                | Gm.      | $[\alpha]_D$ | Gm. | $[\alpha]_D$ | Gm.       | $[\alpha]_D$ | Gm. | $[\alpha]_D$ | Gm. | $[\alpha]_D$ | Gm. | $[\alpha]_D$ |
| ethylbenzene                            | ...      | ...          | ... | ...          | 2         | ...          | ... | ...          | ... | ...          | ... | ...          |
| recovered $\alpha$ -chloro-ethylbenzene | 2        | 0°           | 2   | 0°           | ...       | ...          | 2   | 0°           | 4   | 0°           | 2   | -35.71°      |
| meso-2,3-diphenyl butane                | 2.5      | 0°           | 2.5 | 0°           | } 1       | 0°           | 3.4 | 0°           | 0.5 | 0°           | 2.4 | 0°           |
| d,l-2,3-diphenyl butane                 | 3.5      | 0°           | 3   | 0°           |           |              | 3.1 | 0°           | 1.5 | -4.6°        | 1.3 | +20.29°      |

the postulated mechanism for this photochemical chlorination consists.



The intermediate alkyl radical must undergo racemization in order to obtain inactive products.

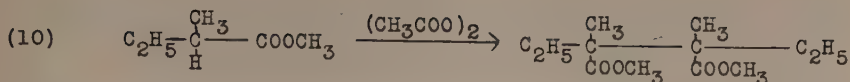
Kharasch, Kuderna, and Urry<sup>8</sup> have studied the reaction of d(+)-methyl-ethyl-acetic acid with acetyl peroxide. They obtained a mixture of the dimeric acid  $\alpha, \alpha'$ -dimethyl- $\alpha, \alpha'$ -diethyl-succinic acid, and its anhydride. Reaction 9 illustrates the over-all reaction.



The monomeric acid (d(+)-methyl-ethyl-acetic acid) recovered, had been only slightly racemized dropping from  $[\alpha]_{\text{D}}^{24} + 17.5^\circ$  to  $[\alpha]_{\text{D}}^{27} + 16.5^\circ$ . The mixture of dimeric acid and anhydride had a rotation of  $[\alpha]_{\text{D}}^{27} + 3.8^\circ$ . The dimeric acid was then esterified forming dimethyl d(+)- $\alpha, \alpha'$ -dimethyl- $\alpha, \alpha'$ -diethyl succinate,  $[\alpha]_{\text{D}}^{24} + 1.82^\circ$ ,  $n_{\text{D}}^{20} = 1.4530$ . From the reaction of methyl-d(+)-methyl-ethyl acetate, the methyl ester of the monomeric acid, with acetyl peroxide they obtained the same dimeric ester,  $[\alpha]_{\text{D}}^{24} + 1.69$ ,  $n_{\text{D}}^{20} = 1.4511$  (equation 10 illustrates this reaction schematically).

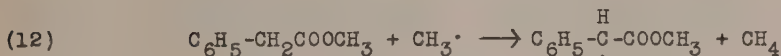
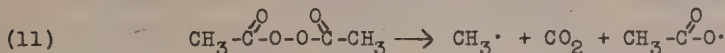
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<sup>8</sup>Kharasch, Kuderna, and Urry, Unpublished results.



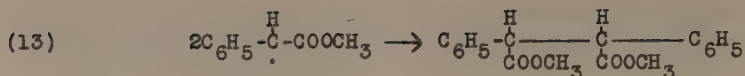
In this case the monomeric ester recovered also showed a slight racemization dropping from  $[\alpha]_{\text{D}}^{24} + 20.93^\circ$ , to  $[\alpha]_{\text{D}}^{24} + 19.58^\circ$ . Since the activity of the optically pure dimeric ester is unknown, it cannot be determined whether the  $+1.69^\circ$  material represents an appreciable amount of optical activity in the dimeric ester. If there were some attack on a beta hydrogen atom instead of the alpha hydrogen atom as shown above, dimethyl-tetramethyl adipate would be the product. The optically active center would be untouched and the reaction product would be expected to have optical activity because of the presence of the product of the beta attack. However, dimethyl-tetramethyl adipate has a hydrogen atom alpha to the carbomethoxyl group and would therefore be expected to racemize on treatment with a strong base, whereas dimethyl- $\alpha, \alpha'$ -dimethyl- $\alpha, \alpha'$ -diethyl succinate, having no alpha hydrogen atoms, would be expected to resist such treatment. Actually the dimeric ester obtained was only slightly racemized by treatment with sodium methoxide in absolute methanol at  $55-70^\circ$  for five hours, dropping from  $[\alpha]_{\text{D}}^{24} + 1.69^\circ$  to  $[\alpha]_{\text{D}}^{24} + 1.44^\circ$ , while methyl- $\alpha$ -methyl- $\alpha$ -ethyl acetate, the monomeric ester, which does contain an alpha hydrogen atom was completely racemized by similar treatment. Further work on this reaction is continuing.

Kharasch, McBay, and Urry,<sup>9</sup> have studied the reaction of acetyl peroxide with certain esters. The product of the reaction is the corresponding dimer formed by linking the alpha carbon atom of one ester to the alpha carbon atom of another. The reaction is considered to have the following mechanism (reactions 11, 12, and 13) illustrated for methyl phenylacetate.

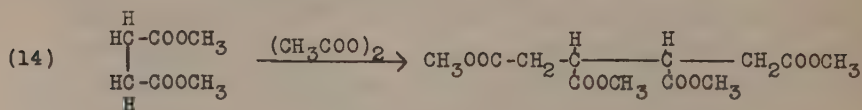



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<sup>9</sup>Kharasch, McBay, and Urry, J. Org. Chem., **10**, 394 (1945).



A similar mechanism has been postulated for the reaction with methyl- $\alpha$ -methyl- $\alpha$ -ethyl acetate discussed above. If the compound being dimerized has an asymmetric carbon atom at the place of dimerization, starting out with a racemic mixture of the monomer and assuming formation of the dimer in all possible combinations, an equal mixture of meso and d,l dimer would be obtained. Even if the monomer did not have an asymmetric carbon atom, but the free radical formed had three different groups attached to it, the dimer would consist of an equal mixture of meso and d,l forms if all possible combinations of forming the dimer were equally probable. This is the case of methylphenylacetate where 50% meso and 50% racemic dimethyl- $\alpha,\alpha'$ -diphenyl succinate is found. In all other cases studied,<sup>10, 11</sup> when meso or racemic dimers could form they were always found in equal quantities. However there is one exception. Kharasch, McBay, and Urry,<sup>12</sup> in the dimerization of dimethyl succinate to form 1,2,3,4-tetracarboxybutane (reaction 14 shows this schematically)



98% of one form was found and only 2% of the other. The configurations are not certain but the 2% form is probably the meso form. Such a result might be due to "steric factors" in the dimerization which makes the dimerization of radicals in certain configurations more probable than in other configurations.

In order to understand more about the dimerization of free radicals and also to determine whether free radicals must be coplanar, a study of the reactions of optically active  $\alpha$ -chloro-

<sup>10</sup> Kharasch, Jensen, and Urry, J. Org. Chem., 10, 386 (1945).

<sup>11</sup> Kharasch, McBay, and Urry, J. Org. Chem., 10, 401 (1945).

<sup>12</sup> Ibid., p. 394.

ethylbenzene with reagents which would produce free radicals at the optically active center was undertaken.

## RESULTS

By the treatment of  $\alpha$ -chloroethylbenzene with propylmagnesium bromide in the presence of cobaltous chloride essentially equal quantities of meso and d,l-2,3-diphenylbutane were obtained. When optically active  $\alpha$ -chloroethylbenzene was used the d,l-2,3-diphenylbutane was found to have a slight activity. Further study showed that this activity could not be due to impurities of optically active  $\alpha$ -chloroethylbenzene or phenylmethylcarbinol from which the  $\alpha$ -chloroethylbenzene had been made. Table 2 lists the results of these reactions.

Acetyl peroxide was decomposed in  $\alpha$ -chloroethylbenzene, yielding a dark colored residue from which could be obtained some solid materials suspected of being 2,3-dichloro-2,3-diphenylbutane. Samples of crystalline material obtained from the residue fractions from the run with optically active materials showed no activity in ethyl acetate solution. The residue from the run with optically active monomer was decolorized with charcoal giving, in ethyl acetate solution, two fractions with the following rotations:  $[\alpha]_D + 0.65^\circ \pm 0.16^\circ$ ,  $C=6.2$ ,  $L=2$ ; and  $[\alpha]_D + 0.71^\circ \pm 0.48^\circ$ ,  $C=2.1$ ,  $L=2$ . The errors are based on an error of  $\pm 0.01^\circ$  in reading the solution and  $\pm 0.01^\circ$  in the zero reading. All attempts to obtain separate meso and d,l-2,3-dichloro-2,3-diphenylbutane from the residue failed. The recovered  $\alpha$ -chloroethylbenzene solvent from the run with optically active material was only slightly racemized dropping from  $[\alpha]_D + 32.03$  to  $[\alpha]_D + 30.70$ .

## DISCUSSION SECTION

Kharasch and Kleiman<sup>13</sup> studied the dimerization to a substituted bibenzyl of a substituted  $\alpha$ -halogenoalkylbenzene through the use of the Grignard reagent and cobaltous chloride. They pre-

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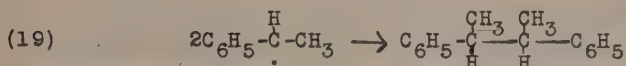
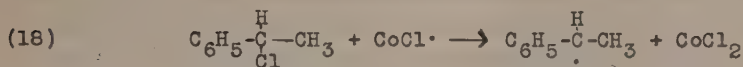
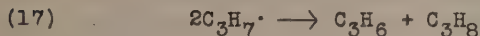
<sup>13</sup>Kharasch and Kleiman, J. Am. Chem. Soc., 65, 491 (1943); cf. Kharasch, Lewis, and Reynolds, ibid., 65, 493 (1943); Kharasch, Engelmann, and Urry, ibid., 66, 365 (1944).



TABLE 2

|                                        | Reaction |       |              |      |            |              |      |            |              |  |
|----------------------------------------|----------|-------|--------------|------|------------|--------------|------|------------|--------------|--|
|                                        | 1        |       |              | 2    |            |              | 3    |            |              |  |
|                                        | Gm.      | Moles | $[\alpha]_D$ | Gm.  | Moles      | $[\alpha]_D$ | Gm.  | Moles      | $[\alpha]_D$ |  |
| Reactants                              |          |       |              |      |            |              |      |            |              |  |
| $\alpha$ -chloroethylbenzene           | 37       | 0.263 | 0°           | 16   | 0.114      | -41.10°      | 14.6 | 0.104      | +37.58°      |  |
| n-propyl magnesium bromide             | ....     | 0.289 | ....         | .... | 0.137      | ....         | .... | 0.13       | ....         |  |
| cobaltous chloride                     | ....     | 0.013 | ....         | .... | 0.006      | ....         | .... | 0.005      | ....         |  |
| Products                               |          |       |              |      |            |              |      |            |              |  |
| 50% propane, 50% propene               | ....     | 0.29  | ....         | .... | 0.14       | ....         | .... | 0.16       | ....         |  |
| recovered $\alpha$ -chloroethylbenzene | 0.8      | 0.006 | 0°           | .... | negligible | ....         | .... | negligible | ....         |  |
| meso-2,3-di-phenylbutane               | 9.12     | 0.043 | 0°           | 4.6  | 0.022      | 0°           | 4.26 | 0.020      | 0°           |  |
| d,l-2,3-di-phenylbutane                | 9.06     | 0.043 | 0°           | 4.4  | 0.021      | - 0.52°      | 5.12 | 0.024      | + 0.32°      |  |

pared hexestrol-dimethyl ether (3,4-dianisylhexane) from anethole hydrobromide. The reaction of  $\alpha$ -chloroethylbenzene with propylmagnesium bromide and cobaltous chloride to form 2,3-diphenylbutane is entirely analogous. A free radical chain reaction is the mechanism for this reaction postulated by the previous authors and is shown here as the best explanation for the reaction under study.



The products found and their yields as described in Table 2 lend support to this mechanism. If the free radical becomes coplanar and if there are no steric effects in dimerization, the dimer should consist of equal quantities of meso and d,l forms even when the monomer is optically active. Reference to Table 2 shows that 50% meso and 50% d,l-2,3-diphenylbutane are actually obtained from the inactive  $\alpha$ -chloroethylbenzene, and also nearly equal amounts of meso and d,l-2,3-diphenylbutane from the runs with active  $\alpha$ -chloroethylbenzene. However, there is a slight activity in the latter d,l-2,3-diphenylbutane. If the results of Ott<sup>14</sup> are to be accepted (see Table 1), the 2,3-diphenylbutane must be considered only slightly active. The fact that this small activity could be due to an impurity was eliminated by the following considerations (see experimental part). No optically active monomer could cause this activity since the monomer contained halogen and the Beilstein copper wire test on the dimer showed no halogen. Furthermore a synthetic mixture of the active monomer and inactive dimer were easily separated by molecular distillation, the method

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<sup>14</sup>Ott, op. cit.; Ott and Behr, op. cit.

used to purify the dimer from the reaction mixtures. The possibility of the presence of an optically active impurity of phenylmethylcarbinol from which the  $\alpha$ -chloroethylbenzene had been made was eliminated by the treatment with pyridine and phthalic anhydride which would remove any alcohols. The dimer had the same rotation before and after treatment. The possibility of the activity being due to any other optically active impurity was eliminated by the fact that recombination and redistillation of the fractions did not change the activity. Any impurities would be expected to fractionate giving different activities in the various fractions.

The small activity found could be due to one of two causes. Either the free radicals maintain their configuration for an appreciable time, that is, are not coplaner; or, the dimerization reaction is one which goes through a mechanism where the intact active  $\alpha$ -chloroethylbenzene is involved, that is, is different than that postulated above. It is not possible to distinguish between these possibilities at present.

Kharasch, McBay, and Urry,<sup>15</sup> studied the dimerization of ethylbenzene to 2,3-diphenylbutane and of p-methoxypropylbenzene to hexestroidimethyl ether by the use of acetyl peroxide. Kharasch, McBay, and Urry<sup>16</sup> have also shown that in acetyl peroxide the attack occurs on hydrogen atoms preferentially to chlorine atoms attached to the same carbon atom. The reaction studied here between acetyl peroxide and  $\alpha$ -chloroethylbenzene to form 2,3-dichloro-2,3-diphenylbutane is analogous with those mentioned above. A free radical mechanism for this reaction has been postulated by the previous authors.<sup>17</sup> This mechanism is shown here for the reaction under study and is well supported by the products obtained.

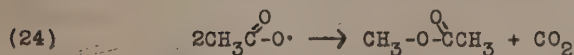
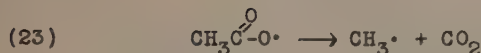
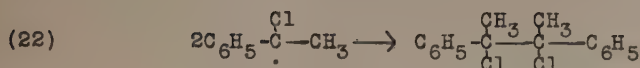
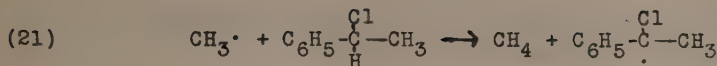



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<sup>15</sup>Kharasch, McBay, and Urry, J. Org. Chem., **10**, 401 (1945).

<sup>16</sup>Ibid., p. 394.

<sup>17</sup>Cf. Kharasch and Gladstone, J. Am. Chem. Soc., **65**, 15 (1943), and the references of nn. 9 (p. 51), 10 and 11 (p. 52).



Since it was not possible to obtain from the residues separately, meso and d,l-2,3-dichloro-2,3-diphenylbutane, it is not known whether the lack of activity in the crystalline material is due to its being pure meso or an inactive product. Also, it is not certain whether the small activity in the none-crystalline fractions of the residue is due to contamination by the monomer or due to active products. It is therefore impossible to draw any conclusions from this reaction. Although, in the case of the reaction of optically active  $\alpha$ -chloroethylbenzene and propylmagnesium bromide in the presence of cobaltous chloride, the product was shown to be optically active.

## EXPERIMENTAL PART

### Reagents

d,l- $\alpha$ -Chloroethylbenzene.--Made according to the procedure described by Kharasch and Kleiman.<sup>18</sup>

Optically active  $\alpha$ -chloroethylbenzene.--Made by the action<sup>19</sup> of thionyl chloride on optically active phenylmethylcarbinol. Eastman's d,l-phenylmethylcarbinol was resolved using brucine and the acid phthalate by the procedure described by Downer and Kenyon.<sup>20</sup>

<sup>18</sup>Kharasch and Kleiman, J. Am. Chem. Soc., **65**, 11 (1945).

<sup>19</sup>McKenzie and Clough, J. Chem. Soc., **103**, 687 (1913).

<sup>20</sup>Downer and Kenyon, J. Chem. Soc., **1939**, 1156.

The Grignard reagent and the cobaltous chloride.--Made by the procedure described by Kharasch, Engelmann, and Urry,<sup>21</sup> with the exception that n-propylbromide was used to prepare n-propyl Grignard.

Acetyl peroxide.--Prepared by the procedure described in Part I of this dissertation.

Reaction of d,l- $\alpha$ -Chloroethylbenzene with Normal-Propylmagnesium Bromide in the Presence of Cobaltous Chloride (Five Mole Per Cent)

The reaction was run according to the procedure described by Kharasch, Engelmann, and Urry<sup>22</sup> and Kharasch, Lewis, and Reynolds<sup>23</sup> with the following exception. The cobaltous chloride (2 grams) was added in three equal portions during the reaction.  $\alpha$ -Chloroethylbenzene (37 grams, 0.26 moles) was dropped into 175 cc. of 1.7 molar normal-propylmagnesium bromide (0.29 moles) in ethyl ether. The gas obtained (7 liters, 100% yield based on the Grignard reagent used) was analyzed by the procedure described by Kharasch, Lewis, and Reynolds,<sup>24</sup> and proved to be 50% propane and 50% propene. A Volhard titration of the wash water for halogen showed 99% reaction. The ether was removed in vacuo at room temperature from the reaction mixture. No attempt was made to investigate the possible formation of any ethylbenzene, styrene, or any other alkyl substituted benzenes. The excess (0.8 grams, 0.006 moles) of  $\alpha$ -chloroethylbenzene (boiling point 36° at 2 mm.) was removed at 1 mm. pressure by raising the temperature of the distillation flask to 100°. The residue, a mixture of oil and solid, was washed with a small quantity of cold methanol and the solid collected on a sintered glass filter. The solid was meso-2,3-diphenylbutane (9.12 grams, 0.043 moles) with a melting point of 124.5-125.5°. The melting point of meso-2,3-diphenylbutane described in the literature is 126°. The oil remaining was distilled in a modified Hickman type molecular still at 10<sup>-5</sup> mm.

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<sup>21</sup>Kharasch, Engelmann, and Urry, J. Am. Chem. Soc., **66**, 365 (1944).

<sup>22</sup>Ibid.

<sup>23</sup>Kharasch, Lewis, and Reynolds, J. Am. Chem. Soc., **65**, 493 (1943).

<sup>24</sup>Ibid.



pressure. The oil was d,l-2,3-diphenylbutane (9.06 grams, 0.043 moles) which boiled at  $95^{\circ}$  at 2 mm. ( $n_D^{20}=1.5539$ ). The physical constants for d,l-2,3-diphenylbutane described in the literature are: boiling point,  $104^{\circ}$  at 1 mm.;  $n_D^{20}=1.5552$ .

Reaction of Levo- $\alpha$ -Chloroethylbenzene with  
Propylmagnesium Bromide in the Presence  
of Cobaltous Chloride

The experiment was performed in a manner similar to that described for the inactive material except that a 20% excess of n-propylmagnesium bromide was added in order to insure complete removal of all optically active  $\alpha$ -chloroethylbenzene. Levo- $\alpha$ -chloroethylbenzene,  $[\alpha]_D - 41.10^{\circ}$  (16 grams, 0.114 moles), 83 cc. of propylmagnesium bromide (0.14 moles), and three-quarters of a gram of cobaltous chloride were used. Three-and-one-half liters of gas (0.14 moles, 100% based on the amount of Grignard reagent used) consisting of 50% propane and 50% propene were obtained. A Volhard titration of the wash water for halogen showed 98% reaction of the Grignard reagent. No  $\alpha$ -chloroethylbenzene was recovered. A solid, meso-2,3-diphenylbutane (4.6 grams, 0.022 moles, m.p.  $125^{\circ}$ ) was obtained. The d,l-2,3-diphenylbutane (4.4 grams, 0.021 moles,  $n_D^{20}=1.5542$ ) was distilled in a modified Hickman type molecular still at  $10^{-5}$  mm. pressure giving 4 fractions having the following rotations: (1)  $[\alpha]_D - 0.54^{\circ} \pm 0.05$ ; (2)  $[\alpha]_D - 0.47^{\circ} \pm 0.05$ ; (3)  $[\alpha]_D - 0.50^{\circ} \pm 0.05$ ; (4)  $[\alpha]_D - 0.58^{\circ} \pm 0.05$ . These fractions were recombined and redistilled giving 2 fractions: (1)  $[\alpha]_D - 0.52^{\circ} \pm 0.05$ , (2)  $[\alpha]_D - 0.47 \pm 0.05$ . All of these fractions gave a negative Beilstein copper wire test for halogen. On refluxing with pyridine and phthalic anhydride for 8 hours followed by thorough washing with HCl,  $\text{Na}_2\text{CO}_3$  solution, and water (a treatment designed to remove alcohols), the oil was recovered. After molecular distillation it had the following rotation  $[\alpha]_D - 0.55^{\circ} \pm 0.05$ . All other fractions from this run including the solid meso compound were completely inactive.

The polarimeter used was instrument 1255 manufactured by Joseph and Jan Fric, Prague; illuminated by a Carl Zeiss sodium vapor lamp. The samples of 2,3-diphenylbutane were placed in a one decimeter tube of 0.9 ml. capacity. Because of the high viscosity of the samples, a maximum probable error of  $\pm 0.05^{\circ}$  is

to be placed on the values obtained for 2,3-diphenylbutane, the polarimeter being capable of higher accuracy for less viscous samples.

Separation of Active  $\alpha$ -Chloroethylbenzene from  
Inactive 2,3-Diphenylbutane

When 0.083 grams of dextro- $\alpha$ -chloroethylbenzene,  $[\alpha]_D + 36.46^\circ$  were mixed with six grams of inactive 2,3-diphenylbutane the mixture which was obtained gave  $\alpha = + 0.51^\circ$  in a one decimeter polarimeter tube. Molecular distillation of the mixture gave three fractions. When measured in a one decimeter polarimeter tube the following values were obtained: (1)  $\alpha = + 1.76^\circ$ , (2)  $\alpha = + 0.04^\circ$ , (3)  $\alpha = 0.00^\circ$ .

Reaction of Dextro- $\alpha$ -Chloroethylbenzene with  
Propylmagnesium Bromide in the Presence  
of Cobaltous Chloride

The experiment was performed in a manner similar to that described for the levo isomer. Used in the reaction were dextro- $\alpha$ -chloroethylbenzene,  $[\alpha]_D + 37.58^\circ$  (14.6 grams, 0.11 moles), 75 cc. of propylmagnesium bromide solution (0.13 moles), and two-thirds of a gram of cobaltous chloride. Three liters of a gas consisting of 50% propane and 50% propene were obtained. No  $\alpha$ -chloroethylbenzene was recovered. A solid, meso-2,3-diphenylbutane (4.26 grams, 0.02 moles, m.p.  $123-5^\circ$ ) was obtained. The d,l-2,3-diphenylbutane (5.12 grams, 0.024 moles,  $n_D^{20} = 1.5544$ ) was subject to molecular distillation yielding three fractions with the following rotations: (1)  $[\alpha]_D + 0.28^\circ \pm 0.05^\circ$ , (2)  $[\alpha]_D + 0.32^\circ \pm 0.05^\circ$ , (3)  $[\alpha]_D + 0.23^\circ \pm 0.05^\circ$ . All other fractions including the solid meso compound were completely inactive.

Decomposition of Acetyl Peroxide in  
d,l- $\alpha$ -Chloroethylbenzene

A solution of acetyl peroxide (4 grams, 0.042 moles) in d,l- $\alpha$ -chloroethylbenzene (24 grams, 0.170 moles) was dropped into a flask held at  $100^\circ$ . A gas collector train of the type described by previous authors<sup>25, 26, 27, 28</sup> was used to collect carbon di-

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<sup>25</sup>Kharasch, McBay, and Urry, J. Org. Chem., 10, 394 (1945).

oxide (2.5 grams, 0.056 moles), methane (1.2 liters, 0.050 moles), and methyl acetate (0.3 grams, 0.004 moles). Upon removal by distillation of the excess d,l- $\alpha$ -chloroethylbenzene (19 grams, 0.135 moles) at 40° and 2 mm. pressure, acetic acid (0.5 grams, 0.135 moles) was collected in the cold trap. A dark colored residue (3.6 grams) was obtained. The residue was taken up in hot 60° ligroin from which some (about 1 gm.) crystalline material separated. The ligroin solutions were decolorized with charcoal. The crystalline material recrystallized from ligroin in diamond-shaped plates which sintered at 140° and melted from 153-170° with gas evolution. Per cent chlorine as obtained by Parr bombs: 25.78%, 25.93%, 26.32%; calculated for 2,3-dichloro-2,3-diphenylbutane ( $C_{16}H_{16}Cl_2$ ); 25.42%. Molecular weight by cryoscopic measurements in benzene solution: 276; calculated for  $C_{16}H_{16}Cl_2$ : 279.

Decomposition of Acetyl Peroxide in  
Dextro- $\alpha$ -Chloroethylbenzene

The reaction was carried out in the same manner as that used with the inactive material described above. Acetyl peroxide (3.8 grams, 0.032 moles) and dextro- $\alpha$ -chloroethylbenzene (12.8 grams, 0.91 moles),  $[\alpha]_D + 32.03^\circ$ , were used. Carbon dioxide (2.2 grams, 0.049 moles), methane (0.9 liters, 0.036 moles), methyl acetate (0.2 grams, 0.003 moles), and acetic acid (0.3 grams, 0.005 moles) were obtained. The dextro- $\alpha$ -chloroethylbenzene (9.3 grams, 0.66 moles) recovered had a slightly lower optical rotation,  $[\alpha]_D + 30.70^\circ$ . A residue (2.6 grams) was obtained. Some crystalline material having the same properties of that obtained from the inactive run was obtained from ligroin solution of the residue. For the polarimetric measurements the ligroin was removed in vacuo and replaced by a minimum amount of ethyl acetate. The solid fractions were completely inactive. The remainder of the residue was decolorized in ligroin solution with charcoal. Two fractions were obtained with the following rotations:  $[\alpha]_D + 0.65^\circ \pm 0.16^\circ$ ,  $C = 6.2$ ,  $L = 2$ ; and  $[\alpha]_D + 0.71^\circ \pm 0.48^\circ$ ,  $C = 2.1$ ,  $L = 2$ . For polarimetry these samples were placed

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<sup>26</sup> Kharasch, Jensen, and Urry, op. cit.

<sup>27</sup> Kharasch, McBay, and Urry, J. Org. Chem., 10, 401 (1945).

<sup>28</sup> Kharasch and Gladstone, op. cit.



in a two decimeter tube of 1.8 ml. capacity. The maximum probable error on these samples is  $\pm 0.02^\circ$  in alpha.

#### SUMMARY AND CONCLUSIONS

1. The reaction of d,l- $\alpha$ -chloroethylbenzene and propylmagnesium bromide in the presence of cobaltous chloride gave meso-2,3-diphenylbutane and an equal quantity of d,l-2,3-diphenylbutane.

2. The reaction of levo- $\alpha$ -chloroethylbenzene with propylmagnesium bromide in the presence of cobaltous chloride gave meso-2,3-diphenylbutane and an equal quantity of lower melting 2,3-diphenylbutane which had an optical activity of  $[\alpha]_D - 0.52^\circ$ .

3. The reaction of dextro- $\alpha$ -chloroethylbenzene with propylmagnesium bromide in the presence of cobaltous chloride gave meso-2,3-diphenylbutane and an equal quantity of lower melting 2,3-diphenylbutane which had an optical activity of  $[\alpha]_D + 0.32^\circ$ .





